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PHOENIX

UNIVERSITY LABORATORY  
OF PHYSICAL CHEMISTRY

RELATED TO  
MEDICINE AND PUBLIC HEALTH



HARVARD UNIVERSITY

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THE ADSORPTION OF AMMONIA BY SILICA GEL.

BY L. Y. DAVIDHEISER AND W. A. PATRICK.

Received May 24, 1921.

The investigation reported here is a continuation of our studies of adsorption of gases and vapors by silica gel. In Göttingen with Zsigmondy the adsorption of ammonia, sulfur dioxide and carbon dioxide of silica gel was studied. Since then many improvements in experimental technique have been introduced, as well as radical modifications of the theoretical treatment of the experimental results. The experimental method and an outline of our theoretical views have been given in a paper dealing with the adsorption of sulfur dioxide.<sup>1</sup>

The adsorption of ammonia was studied for a number of reasons. In the first place, this gas, in the measurements made in Göttingen, was found to be more strongly adsorbed than sulfur dioxide although the latter exhibits a higher critical temperature. In the second place, our previous measurements indicated that the behavior of ammonia was anomalous from the standpoint of the rate at which equilibrium was reached. Again, ammonia is extremely soluble in water and it was therefore hoped that by a careful study of its adsorption by silica gel, light would be thrown on the question as to the nature of the small amount of water that is always associated with the gel. Furthermore, in am-

<sup>1</sup> MacCavack and Patrick, *THIS JOURNAL*, 42, 946 (1920).

monia we have a gas that has been the subject of numerous careful investigations, and as a result the physical constants, such as vapor pressure, density and surface tension, are very accurately known. This latter point is especially important inasmuch as a knowledge of the above constants is necessary for the testing of our theoretical views as to the course of the adsorption.

In the following measurements of the adsorption of ammonia by silica gel, it will be shown that this gas is not anomalous in its behavior, either from the standpoint of the extent or the rate of the adsorption, the earlier discrepancies being due to the uncertain water and acid content of the gel. Especial study was made of the influence of the water content of the gel on the adsorption, and it was found that small differences produced large variations in the adsorptive ability of the material.

**Apparatus.**—The experimental method has been described in detail by MacGavack and Patrick.<sup>1</sup> To give an idea of the precision attained, it may be stated that the volume of ammonia was measured to within 0.005 cc., the pressure to within 0.03 mm., and the temperature of the thermostat regulated so as not to vary more than 0.05°.

**Material.**—The ammonia used was purified liquid ammonia. Commercial ammonia was treated with metallic sodium for one week, and the accumulated gas allowed to escape at intervals of 12 hours. The purified sample was tested by allowing a small stream of the gas to bubble into sulfuric acid contained in a gas buret for 10 minutes; as no residue was shown by this procedure it was assumed that the ammonia was free from permanent gases.

The silica gel was an ordinary commercial sample that was further purified by treatment with nitric acid and a thorough washing with distilled water. When dried in a vacuum of 1 to 5 mm. at a temperature of 300° for 3 hours the gel still contained 5.21% of water, and furthermore an appreciable amount of nitric acid, to which reference will be made later.

**Procedure.**—The adsorption apparatus was evacuated by means of a rotary oil pump and a Gaede mercury pump, connected in series. Before any gel was put into the adsorption bulb, the apparatus was thoroughly evacuated and then swept out with ammonia and evacuated again until the MacLeod gage showed no pressure after standing under a vacuum for 48 hours. The gel was weighed in the adsorption bulb, which was then directly attached to the apparatus by means of a ground joint, and sealed by mercury. The pumps were always started before the stopcock between the adsorption bulb and the main apparatus was opened, so that the air in the bulb would have less chance to become adsorbed on the walls of the apparatus. The heating of the adsorption bulb was started at the same time, care being taken not to heat the gel to a higher temperature

than that at which it was prepared, so that the water content might not be disturbed. The evacuation was continued until the MacLeod gage showed no pressure, usually from 3 to 8 hours, at a temperature from 290° to 300°.

In the beginning it was found almost impossible to make two determinations that would agree. After a considerable number of measurements had been made at 30°, a few were found to check fairly well. However, a number of measurements made at 40° showed that the gel exhibited greater adsorptive ability at this temperature than at 30°. Such inconsistent and disturbing results led us to stop and thoroughly inspect our apparatus and method of procedure. The apparatus was first examined for leaks. It was thoroughly evacuated and allowed to stand for one week, at the end of which the MacLeod gage showed no increase of pressure. The ammonia was again examined and no foreign gases found. Another series of measurements was made at 30° in which great care was taken that all manipulations should be as nearly identical as possible. The electric furnace, in which the adsorption bulb was heated during evacuation, was kept constant and evacuation continued for exactly the same length of time. Under these conditions checks could be made with but little variation. This proved that the gel did not remain constant

TABLE I  
EXPERIMENTS AT 0°, 30°, 40° AND 100°

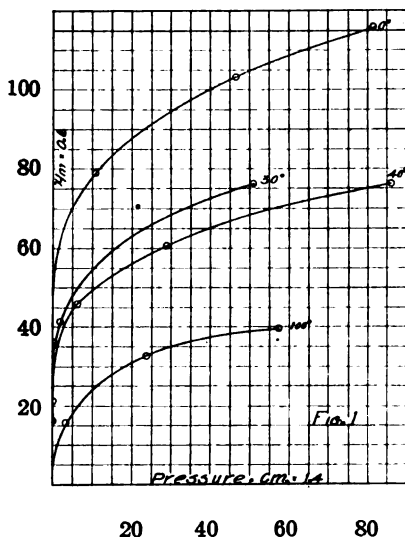
Expt. XX			
Temp., 30°; H <sub>2</sub> O content, 4.93%; Wt. of gel, 0.5739 g.; <i>D</i> , 0.5939; $\sigma$ , 18.03; 1/ <i>N</i> , 0.2103; <i>K</i> , 57.30; <i>P</i> <sub>o</sub> , 874.90.			
<i>P</i>	<i>X/M</i>	<i>V</i>	<i>P</i> $\sigma$ / <i>P</i> <sub>o</sub>
0.07	26.82	0.034	0.001443
1.009	68.05	0.087	0.020792
37.726	126.66	0.161	0.683757

Expt. XXIII			
Temp., 40°; H <sub>2</sub> O content, 4.93%; Wt. of gel, 0.5730 g.; <i>D</i> , 0.5769; $\sigma$ , 16.70; 1/ <i>N</i> , 0.2093; <i>K</i> , 53.53; <i>P</i> <sub>o</sub> , 1165.80.			
<i>P</i>	<i>X/M</i>	<i>V</i>	<i>P</i> $\sigma$ / <i>P</i> <sub>o</sub>
0.218	36.42	0.050	0.003123
4.026	77.03	0.101	0.057672
20.987	101.06	0.133	0.300622
61.632	126.25	0.166	0.882887
<i>P</i> = equilibrium pressure in cm. of mercury.			
<i>X/M</i> = cc. of ammonia under standard conditions adsorbed per g. of gel.			
<i>V</i> = cc. of liquid ammonia adsorbed.			

Expt. XXV			
Temp., 0°; H <sub>2</sub> O content, 4.93%; Wt. of gel, 0.5744 g.; <i>D</i> , 0.6389; $\sigma$ , 25.94; <i>P</i> <sub>o</sub> , 322.10; 1/ <i>N</i> , 0.2116; <i>K</i> , 82.40.			
<i>P</i>	<i>X/M</i>	<i>V</i>	<i>P</i> $\sigma$ / <i>P</i> <sub>o</sub>
0.153	58.77	0.070	0.012321
8.116	123.47	0.147	0.654614
33.494	168.59	0.200	2.697404
58.653	191.99	0.228	4.723902

Expt. XXIX			
Temp., 100°; H <sub>2</sub> O content, 4.93%; Wt. of gel, 0.5737 g.; <i>D</i> , 0.4589; $\sigma$ , 6.5; 1/ <i>N</i> , 0.2885; <i>K</i> , 23.07; <i>P</i> <sub>o</sub> , 4693.40.			
<i>P</i>	<i>X/M</i>	<i>V</i>	<i>P</i> $\sigma$ / <i>P</i> <sub>o</sub>
2.147	27.05	0.04473	0.00276
13.805	52.22	0.08636	0.01912
41.016	66.62	0.11017	0.05681
<i>P</i> <sub>o</sub> = vapor pressure of liquid ammonia.			
<i>D</i> = density of liquid ammonia.			
$\sigma$ = surface tension of liquid ammonia.			

during evacuation, and especially was this true when the pumps were run for different lengths of time. All the experiments recorded in this paper were made under conditions that allow exact duplication.



In Table I Experiments XX, XXIII, XXV and XXIX are recorded the results of the measurements made at 0°, 30°, 40° and 100°. These results are shown graphically in Fig. 1. Equilibrium was usually reached in from 15 to 30 minutes; nevertheless the ammonia was allowed to remain in contact with the gel for at least 2 hours. As more ammonia was introduced and the pressure increased, the time required to reach equilibrium also increased. If equilibrium was not reached within 2 hours after the introduction of the first amount of ammonia, it served as an indication that the air had

not been completely removed from the apparatus. It was found that 3 hours' evacuation with the adsorption bulb heated to 290° was sufficient to remove all the air. All the determinations were made under these conditions. After this treatment it was found that the gel lost 0.28% of its water content. When this treatment was continued for 8 hours 0.487% of the water was removed. The gel upon analysis was found to contain 0.437% of nitric acid, equivalent to 5.23 cc. of ammonia. Of course as the gel lost some of its water content some of the acid also was lost.

Inasmuch as our preliminary measurements showed that the water content of the gel was a most important factor in determining the extent of the adsorption, an effort was made to prepare a gel of low water content. It has previously been thought that the presence of the water was very closely associated with the structure of the material and the removal of the water below 2% was considered undesirable. The subsequent results, however, indicate that such views are unsound and that it is possible to obtain a gel possessing the proper adsorptive structure having only 0.33% of water.

A gel containing 0.33% of water was prepared by heating it in a Pyrex glass tube through which a current of dry air was passed. The tube was gradually heated with a Bunsen flame for 1 hour, and then in the flame of the blast lamp for 2 hours to the fusion point of Py-

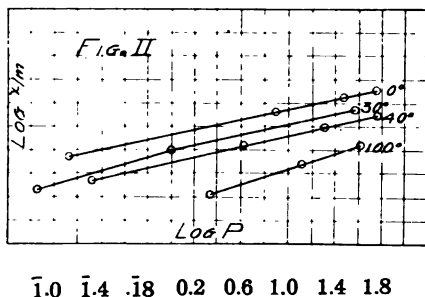
rex glass. During this process the gel became perfectly clear and colorless.

After this treatment the gel was tested for its ability to adsorb ammonia. It was rather surprising to find that it was still a good adsorbent for ammonia, adsorbing on an average about 53 cc. less per gram than it did before this drastic treatment. Two isotherms were made, one at 0° and one at 30°. Fig. 3 shows the graph of these determinations as compared with those made before dehydrating the gel. Table II, Experiments XXXI and XXXV show the experimental results.

TABLE II  
ACTION OF GEL AFTER HEAT TREATMENT

Expt. XXXI				Expt. XXXV			
Temp., 30°; H <sub>2</sub> O content, 0.33%; Wt. of gel, 0.5739 g.; D, 0.5939; $\sigma$ , 18.03; 1/N, 0.2487; K, 21.33; P <sub>0</sub> , 874.90.				Temp., 0°; H <sub>2</sub> O content, 0.33%; Wt. of gel, 0.5739 g.; D, 0.6389; $\sigma$ , 24.94; 1/N, 0.3948; K, 28.765; P <sub>0</sub> , 322.10.			
P	X/M	V	P $\sigma$ /P <sub>0</sub>	P	X/M	V	P $\sigma$ /P <sub>0</sub>
1.293	24.49	0.03113	0.026646	3.391	47.85	0.05684	0.273091
8.653	46.00	0.05878	0.178021	6.763	61.35	0.07287	0.544651
18.933	57.08	0.07294	0.390173	13.964	80.54	0.09567	1.124572
36.600	73.50	0.09392	0.754265	46.056	127.50	0.15145	3.708976
59.697	83.01	0.10608	1.23024	61.365	145.44	0.17276	4.941874

It is necessary to mention a phenomenon that was observed with the measurements made at 100°. After 33.64 cc. of ammonia had been brought over 0.5741 g. of gel and the pressure had reached a value of 287.35 mm., it was noticed that there was a gradual increase in the pressure. This increase in pressure continued until at the end of 9 days the pressure in the apparatus was 471.40 mm. Upon cooling the gel to 0°, the pressure immediately dropped to 4.53 mm., while heating again to 100° caused an immediate rise in pressure to the value of 471.40 mm. That this phenomenon is in some way associated with the water of the gel is indicated by the fact that no such behavior as outlined above was exhibited with the gel containing only 0.33% of water.



### Discussion of Results.

The various isotherms may be very accurately represented by the ordinary empirical adsorption formula,  $X/M = KP^{1/N}$ . In Fig. 2 are plotted the logarithms of  $X/M$  against  $P$ , and from the straightness of the lines it is apparent that the above formula accurately reflects the

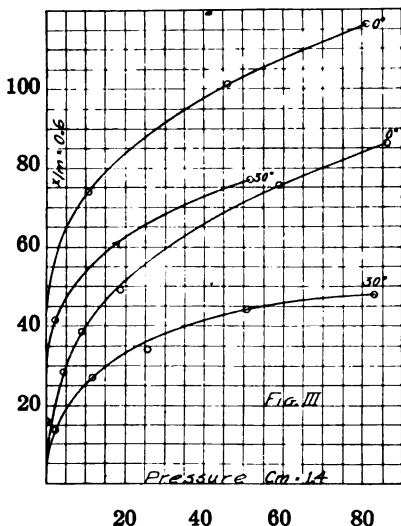
experimental data. Inasmuch as the sulfur dioxide was also well represented by the same relationship, the comparison of the behavior of ammonia and sulfur dioxide is greatly facilitated by use of the values of  $K$  at the same temperature. In the following table are given the values of  $K$  for sulfur dioxide and ammonia obtained with a gel of approximately the same water content, 4.8%.

	NH <sub>3</sub> $K$	SO <sub>2</sub> $K$
0°	82.40	29.14
30°	57.30	12.93
40°	53.53	9.75
100°	23.01	1.12

Inasmuch as the significance of  $K$  is the number of cubic centimeters of gas adsorbed by 1 g. of gel at a pressure of 1 cm., it is apparent that ammonia is more strongly adsorbed than sulfur dioxide by this particular sample of gel.

That this result is due to the larger solubility of ammonia in water, is shown by the fact that the value of  $K$  for ammonia at 0° decreased from 82.40 to a value of 28.76 when the water content was reduced from 4.88% to 0.33%.

While it is true that the adsorption of sulfur dioxide is lessened by a diminution of the water content of the gel, the effect here is not so pronounced as in the case of ammonia. It will be observed that with a gel containing 0.33% water content, the adsorption of ammonia is lower than that of sulfur dioxide in a gel containing 4.87% water. It is our belief that with an anhydrous gel the adsorption of ammonia will be found to be in accordance



with its ease of condensation as expressed by its critical temperature.

The above results for ammonia must also be corrected for the acid that is present in the gel. In the beginning it was thought that prolonged washing with distilled water was sufficient to remove all acid, especially inasmuch as the acid diffuses readily through the gel when in the state that it is when washed. Nevertheless, upon collecting the liquid that is driven off from a gel containing 5.21% water by heating to 800–900°, the same was found to require 0.653 cc. of 0.1066  $N$  alkali for the neutralization per gram of gel. This acid would probably not exert an appre-

cial effect upon an acidic gas such as sulfur dioxide, but would materially affect the adsorption of ammonia.

The above facts illustrate the great need for care when generalizations are drawn concerning adsorption. It is apparent that the amount of ammonia that the gel is capable of taking up depends not only on the capillary structure of the gel, but in addition upon the water and acid content. Before generalizations as to the effect of capillarity on adsorption may be drawn, it is necessary to allow for the solubility of the gas in the water and the amount of ammonia that combines with the acid present.

If instead of expressing the weight of ammonia taken up by a unit weight of gel under a certain pressure, the volume of liquid ammonia adsorbed per gram of gel under its condensation pressure is used, all the isotherms fall on a smooth curve which may be expressed by the equation

$V = K \left( \frac{P_\sigma}{P_0} \right)^{1/N}$ . These results are shown in Fig. 4, where will be found

plotted the logarithms of the volume of ammonia adsorbed against the logarithms of the condensing pressures ( $P_\sigma/P_0$ ).

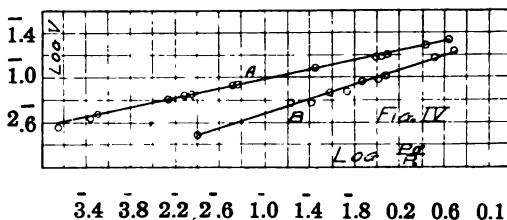
A similar result was obtained with the sulfur dioxide measurements where the values of  $K$  and  $1/N$  were 0.1039 and 0.447, respectively. In the case of ammonia with a gel of 4.88% water content, the equation becomes  $V = 0.1679 \left( \frac{P_\sigma}{P_0} \right)^{0.2105}$ ; while with a gel of 0.33% water content

$K$  has the value of 0.0955 and  $1/N$  of 0.3588.

At first thought it may be considered strange that the above formula should apply to the adsorption of ammonia when we consider the very large portion of the ammonia that is dissolved in the water of the gel. This behavior is immediately explained, however, from the fact that the solubility of ammonia in water may be expressed by the same formula that is used to express the results of the adsorption of ammonia by silica gel. In other words, as shown by measurements made in this laboratory, the solubility of ammonia in water is well represented by the formula,

$$V = K \left( \frac{P_\sigma}{P_0} \right)^{1/N}$$

It has also been shown that the solubility of sulfur dioxide in water may be well represented by the above formula where  $K$  equals 0.0123 and  $1/N$  equals 0.91. It is therefore possible to calculate the adsorption





due to the capillary structure alone by correcting, with the aid of the above formula, for the amount of gas dissolved in the water of the gel. Applying this formula,  $V = K \left( \frac{P_\sigma}{P_0} \right)^{1/N} + 0.048 K' \left( \frac{P_\sigma}{P_0} \right)^{1/N'}$ , to the measurements of ammonia made with the gel containing 4.8% water, the value of  $K$  becomes 0.1147. Doing the same with the measurements of sulfur dioxide, we find that the mean value for  $K$  does not differ much from 0.1038. The  $K$  for the anhydrous gel is 0.0955. From these experiments we see that the amount of different gases adsorbed due to capillarity is in good agreement.

### Summary.

1. The adsorption of ammonia by silica gel has been measured under various pressures at 0°, 30°, 40°, and 100°.
2. The influence of the water content of the gel on the adsorption has been studied.
3. It has been shown that the adsorption of ammonia may be satisfactorily explained on the basis of capillary condensation, provided corrections are made for the amount of the gas that dissolves in the water.

BALTIMORE, MARYLAND.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA.]

## A STUDY OF THE SYSTEM AMMONIA : MAGNESIUM : MERCURY. THE FORMATION OF MAGNESIUM HEXAMMONIATE.

By ALBERT G. LOOMIS.

Received August 4, 1921.

### Introduction.

The object of this investigation was to study the properties of the three-component system ammonia : magnesium : mercury, and to establish the constitution of the solid phase which separates when dilute magnesium amalgams are allowed to absorb ammonia. The separation of this solid phase was first observed by the late Dr. William Argo, and at his suggestion this work was undertaken. It was of interest to determine whether mercury is an essential constituent of the solid phase, and whether a compound of magnesium and ammonia, but containing no mercury, could be prepared corresponding to calcium hexammoniate  $\text{Ca}(\text{NH}_3)_6$ , calcium hexammoniate, discovered and studied by Kraus.<sup>1</sup> A study of the properties of this compound, together with such groups as methyl mercury, and solutions of the alkali metals in anhydrous ammonia has led Kraus to highly important conclusions regarding the theory of the metallic state and the mechanism of metallic conduction.

<sup>1</sup> Kraus, *THIS JOURNAL*, 29, 1557 (1907); 30, 653 (1908).

The metals which have been reported to be soluble in liquid ammonia are: sodium and potassium,<sup>2</sup> lithium,<sup>3</sup> rubidium and cesium,<sup>4</sup> calcium,<sup>5</sup> barium,<sup>6</sup> and strontium.<sup>7</sup> Magnesium goes into solution very slowly; if, however, it is first treated with a solution of an ammonium salt in liquid ammonia, allowing some hydrogen to be evolved, and then washed free of the ammonium salt, immediate solution takes place. Compounds of metals with ammonia of the following formulas have been reported:  $\text{NaNH}_2$ ,  $\text{KNH}_2$ ,<sup>8</sup>  $\text{LiNH}_2$ ,  $\text{Ca}(\text{NH}_2)_2$ ,<sup>5</sup>  $\text{Ba}(\text{NH}_2)_2$ ,<sup>9</sup> and  $\text{Sr}(\text{NH}_2)_2$ .<sup>10</sup> Kraus,<sup>1</sup> however, proved by phase rule criteria that sodium, potassium, and lithium do not form compounds with liquid ammonia, but true solutions. He found also that the compound with calcium was not calcium tetrammoniate as reported by Moissan, but calcium hexammoniate. This compound is prepared by allowing excess ammonia to dissolve calcium metal and pumping off ammonia to the dissociation pressure of the compound.

Several cases are known of compounds of two metals existing in liquid ammonia. Joannis<sup>11</sup> found that lead dissolves in ammonia solutions of sodium, two atoms of lead being present to one atom of sodium in solution. Other compounds reported by Joannis have the formulas  $\text{Na}_3\text{Sb}$ ,  $\text{NaPb}$ ,  $\text{NaPb}_4$ ,  $\text{Na}_2\text{Bi}$ ,  $\text{KPb}_2$ , etc. According to Peck,<sup>12</sup> Kraus has found that further reactions take place with an excess of the heavy metal, forming compounds richer in the heavy metal. Smyth<sup>13</sup> has studied the solutions of lead in sodium solutions in ammonia and reached the conclusion that there is an equilibrium between  $\text{Pb}_2^-$  and  $\text{Pb}_3^-$  in the presence of metallic lead.

Lebeau<sup>14</sup> has reported that trilithium antimonide  $\text{Li}_3\text{Sb}$  is soluble in liquid ammonia. Kraus<sup>1</sup> has found that lead is soluble in ammonia solutions of potassium, giving a green color, and that tin is soluble in ammonia solutions of sodium, giving a red color. According to Peck,<sup>12</sup> Kraus has found also that tin, tellurium, selenium, and sulfur react and form compounds with solutions of the alkali metals in ammonia.

**Description of the Solid Phase.**—The crystals which are formed when magnesium amalgam absorbs ammonia have a bright metallic luster. The absorption of ammonia is exceedingly slow, probably on account of the slowness with which ammonia penetrates below the surface of the solid phase; the reaction is complete within 10 to 15 days. The adsorption of ammonia in all cases was allowed to take place at room temperature in a sealed tube in order that the high pressure of the ammonia (about 8 atmospheres at room temperature) might hasten the reaction. The crystals are slowly decomposed when exposed to air, or when the pressure of the ammonia vapor is reduced below about 2 atmospheres. The

<sup>2</sup> Weyl, *Ann. Phys.*, **121**, 601 (1864).

<sup>3</sup> Seely, *Chem. News*, **23**, 169 (1871).

<sup>4</sup> Moissan, *Compt. rend.*, **136**, 1177 (1903).

<sup>5</sup> Moissan, *ibid.*, **127**, 685 (1898).

<sup>6</sup> Guntz, *ibid.*, **133**, 874 (1901).

Mentrel, *ibid.*, **135**, 740 (1902).

<sup>7</sup> Guntz, *ibid.*, **133**, 1209 (1901).

<sup>8</sup> Joannis, *ibid.*, **109**, 900 (1889).

<sup>9</sup> Mentrel, *ibid.*, **135**, 790 (1902); *Bull. soc. chim.*, **29**, 493 (1903).

<sup>10</sup> Roederer, *Compt. rend.*, **140**, 1252 (1905).

<sup>11</sup> Joannis, *ibid.*, **113**, 795 (1891).

<sup>12</sup> Peck, *THIS JOURNAL*, **40**, 335 (1918).

<sup>13</sup> Smyth, *ibid.*, **39**, 1299 (1917).

<sup>14</sup> Lebeau, *Compt. rend.*, **134**, 284 (1902).

amalgam may be made to remain semi-liquid or completely solid, depending on the amounts of ammonia and magnesium added. Amalgams richer in magnesium than 0.15% become completely solid with excess of ammonia, while more concentrated amalgams become completely solid if more than 0.035 mol. of ammonia is added per 100 g. of amalgam. Even with the most dilute amalgams crystals of the compound separate, indicating their small solubility in the excess of amalgam. In practically all cases amalgams were used in which there was no solid phase of magnesium present.

*Solubility of Magnesium in Mercury.*—No data could be found on the solubility of magnesium in mercury, so this value was determined. Three determinations gave 0.323%, 0.322% and 0.324% of magnesium at room temperature (23°). These amalgams were made by warming pure mercury with excess magnesium *in vacuo* and, after cooling to room temperature, were allowed to stand for several days, with frequent shaking to avoid supersaturation. The saturated amalgam was filtered through a plug of glass wool by means of hydrogen pressure into an evacuated receiving bulb, which was sealed off *in vacuo* when a sufficient amount had filtered. The magnesium content was determined by the method of Gooch and Austin,<sup>15</sup> the mercury by difference.

#### Apparatus and Materials Used.

All ammonia used was obtained from large stock cylinders, dried with sodium, and kept in glass containers as a saturated solution in ammonium nitrate, known as Diver's solution. The ammonium nitrate had been previously dried with extreme care by heating with a boiling-water jacket for some hours *in vacuo*. Before using, the ammonia was always dried again with sodium, so that the final product was very pure after the several distillations and drying. All mercury used was purified by the Hulett method and stored in a glass container by distilling *in vacuo*. The magnesium was of very pure quality and carefully freed from all oxide. Vacuum stopcocks were used throughout the investigation, as were Trimount oil vacuum pumps capable of rapid exhaustion to 0.001 mm. of mercury. All glass containers and connecting tubes were thoroughly cleaned with strong caustic soda solution, chromic acid, and pure water. Before filling with the amalgams the containers were heated *in vacuo* with a free flame almost to the softening point of the glass. After evacuation for some time the containing vessel was filled with dry hydrogen and again evacuated. The hydrogen was made and dried with sodium-potassium alloy, as recommended by Hine.<sup>16</sup> This latter refinement was necessary on account of the extreme reactivity of magnesium amalgam with traces of moisture and air that remain on the surface of the glass. Using the precautions described above, amalgams were obtained free of all traces of oxide scum.

An important part of the containing tubes was an arrangement which we may call a "sealed stopcock," which was used by Lewis and Lacey<sup>17</sup> (see Fig. 1). It is impossible to keep liquid ammonia quantitatively at room temperature by means of an ordinary stopcock, and throughout the entire investigation this arrangement was used. The containing tube was attached at (C), while (E) was attached to the exhaustion pump.

<sup>15</sup> Gooch and Austin, *Zeit. anorg. Chem.*, 20, 121 (1899).

<sup>16</sup> Hine, *THIS JOURNAL*, 39, 882 (1917).

<sup>17</sup> Lewis and Lacey, *ibid.*, 37, 1976 (1915).

After thorough evacuation stopcock (D) was closed. By heating the plug (B) of low-melting glass and pulling on the platinum wire (P) the small tube could be broken off at a file mark which had been made previous to making the ring seal at (R).

### Vapor-pressure Measurements.

Vapor-pressure measurements were made at  $0^\circ$  to study the form of the curve obtained by plotting vapor pressures of ammonia as ordinates against amounts of ammonia removed as abscissas. Our object was to obtain the solid compound just free of excess liquid ammonia in order to analyze it. Dilute amalgams were made, an excess of dry liquid ammonia was introduced, and the sealed tubes were allowed to stand for 10 days or longer. The containing tubes were made with several arms in order to have as much surface of compound exposed as possible, and were shaken at intervals in order to hasten the attainment of equilibrium. A large glass spiral made from tubing of small bore was used to gain flexibility and permit shaking without the use of rubber connections. The ammonia vapor was removed by allowing it to expand into an evacuated bulb of about 15cc. capacity. Vapor pressures were recorded as soon as the liquid ammonia phase had entirely disappeared. It was found in a separate experiment that the liquid ammonia phase was pure and contained no dissolved material. Consequently no vapor-pressure measurements were necessary while this phase was present, since the system was behaving practically as a one-component system.

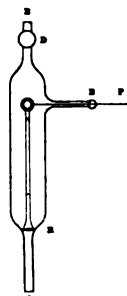


Fig. 1.

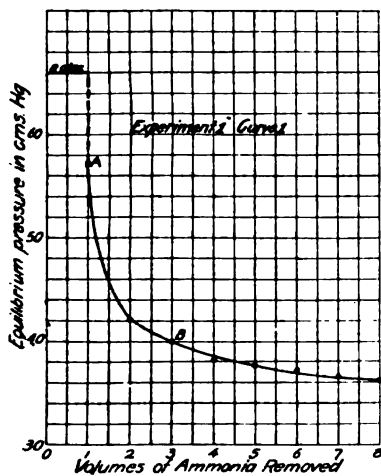


Fig. 2.

due to its decomposition. The pressures obtained were plotted against

<sup>18</sup> Kraus (Ref. 1) experienced the same difficulty in his work on the vapor pressure of  $\text{Ca}(\text{NH}_2)_2$ .

volumes of ammonia removed and Curve 1, Fig. 2 obtained. In this experiment about 5.0% of the crystals was decomposed by removing ammonia. This estimate was made from results which were obtained later in the investigation regarding the composition of the solid. In a second experiment, identical with the first one, more ammonia was removed, estimated to decompose about 15% of the solid. These results when plotted give a similar curve to that of Experiment 1, although the curves cannot be directly superimposed, since the concentrations of the amalgams in the two experiments were not identical. A summary of results is given in the following table.

TABLE I  
VAPOR-PRESSURE MEASUREMENTS  
All Measurements at 0°

Vols. of Amm. Vapor Removed	1	2	3	4	5	6	7	8	18
Equilib. V.P. in Cm. of Hg.									
Expt. 1.....	57.3	42.2	40.0	38.1	37.7	37.3	36.7	36.1	....
Expt. 2.....	67.1	....	48.0	....	....	42.1	38.9	....	27.6

**Discussion of Curves Obtained.**—From the form of the curve obtained, showing gradually decreasing pressures as ammonia is removed, it is concluded that there are only two phases present besides the vapor phase, one at least of which is variable in composition. The variable phase is almost certainly the amalgam, the solid compound being the second phase. The pressures do not become constant as soon as the solid begins to decompose; for instance, at point B of Curve 1 (Fig. 2) the pressure rose from 9.2 cm. to 40.0 cm. of mercury after some hours. This behavior was repeated as more ammonia was removed. Since the pressures do not become constant as soon as the solid begins to decompose this method of analysis is eliminated. There is also no evidence from the study of the curves that the solid maintains constant composition, and this point was next investigated by direct analysis. Since from A to B on the curve the composition is changing too rapidly, we will choose for analysis the region in which the vapor pressure has assumed a more constant value.

#### Determination of Ratio of Magnesium to Ammonia in Crystals.

**Method of Making Amalgams.**—In order to determine the number of mols of ammonia combined with one gram atom of magnesium, amalgams of widely differing concentrations were made and excess of liquid ammonia added.

Magnesium, free of oxide, was weighed and introduced into Tube C (see Fig. 3). After the containing tube was sealed to the apparatus it was evacuated, heated with a free flame almost to the collapsing point of the glass, filled with dry hydrogen, and again evacuated and heated. Mercury which had been distilled in the reservoir (W) *in vacuo*

was allowed to fill the evacuated pipet (P) up to the zero mark on the capillary stem, the level of mercury being adjusted at will by means of hydrogen pressure through the stopcock above the stem. The pipet as well as the stem above the zero mark had previously been calibrated very carefully by introducing the mercury from W as described, and allowing it to run into a weighing bulb attached to the glass arm (N). By turning the 3-way stopcock (S) the pipet was allowed to empty into the containing tube (C). Any small droplets of mercury adhering to the glass were forced into C by means of hydrogen pressure. The containing tube was now shaken until all the magnesium had dissolved and excess liquid ammonia introduced from Tube T by immersing the bulb of C in a cooling mixture such as carbon dioxide snow and ether. The ammonia had previously been condensed into Tube T from the Diver's solution in order to dry it thoroughly with metallic sodium. Tube C was now sealed off at M and N under reduced pressure.

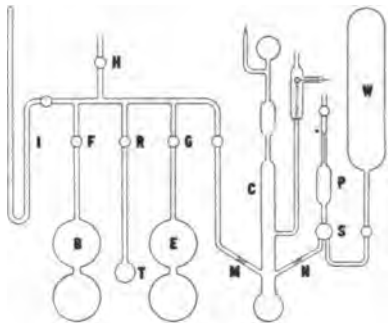


Fig. 3.

**Decomposition of Crystals.**—After the tubes had stood for several weeks at room temperature, and complete absorption of ammonia had taken place, they were sealed to the apparatus shown in Fig. 4. The sealed stopcock was thoroughly evacuated through Tube C, Stopcock B was closed, the containing tube cooled in a bath of liquid ammonia, and the small tube broken off at E. The excess liquid ammonia was allowed to escape through Tube A under a trap of mercury. After the excess liquid ammonia had all evaporated, the entire system was evacuated, which removed all ammonia vapor from above the crystals, shown by a low pressure on the gage G. Stopcock D was then closed and the crystals decomposed by heating and cooling Tube T in carbon dioxide snow and ether. After the decomposition was complete, Tube T was sealed off and the weight of ammonia determined. The volume of the containing and side tubes was next determined and the amount of ammonia vapor not condensed in T was calculated from the volume and the pressure as shown on the gage (G). This weight was added to the weight of the liquid ammonia condensed in T.

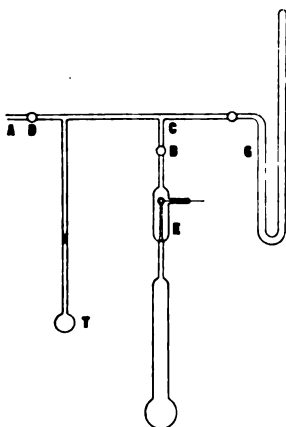


Fig. 4.

The results are summarized in Table II.

It is seen from the table that the ratio of the number of gram atoms of magnesium to mols of ammonia is approximately 1 to 6 for amalgams of widely differing concentrations. Probably some ammonia vapor is enclosed mechanically in the crystals which would cause uniformly high results. Therefore we may safely

conclude that the formula of the compound is  $\text{Mg}(\text{NH}_3)_6\text{Hg}_x$ . The problem of determining whether mercury is combined in the crystal now presents itself.

TABLE II  
RATIO OF AMMONIUM TO MAGNESIUM IN CRYSTALS

Expt.	Wt. of Mg. per 100 g. of Hg. G.	Gram atoms of Mg.	Mols of ammonia combined	Mols of ammonia combined with 1 g. atom of Mg.
1	0.0508	0.00209	0.0128	6.12
2	0.0536	0.00201	0.0140	6.33
3	0.0813	0.00335	0.0205	6.12
4	0.0976	0.00401	0.0253	6.32
5	0.3122	0.01284	0.0764	5.95
6	0.3768	0.01550	0.0972	6.27
7	0.4282	0.01752	0.1056	6.02
8	0.4604	0.01892	0.1166	6.16
9	0.5118	0.02200	0.1330	6.04

### Determination of Combined Mercury in the Crystals.

**General Methods.**—The chief difficulty to overcome in the determination of the constitution of solid phases which separate from amalgams is due to the fact that it is impossible to completely free the solid phase of adhering mother amalgam.

Kerp<sup>19</sup> and Kerp, Böttger, Winter and Iggena<sup>20</sup> determined the composition of crystals from amalgams by removing the mother amalgam on a Gooch crucible. This method was later shown to give erroneous results due to incomplete removal of amalgam. Centrifugal machines also give imperfect removal of the mother liquor (C. van Eyk<sup>21</sup>). A. van Bijlert<sup>22</sup> and Bancroft<sup>23</sup> have discussed the method of adding a reference substance to the mother liquid which does not form part of the crystal. From an analysis of the crystals for the reference substance the amount of adhering mother liquor may be calculated. Bijlert<sup>22</sup> used silver as the reference metal in his study of the tin-antimony alloys. Van Heteren<sup>24</sup> made use of cadmium as reference metal in the study of tin amalgams. Bancroft<sup>23</sup> has discussed the method of analyzing the filtrate to determine by indirect means the constitution of the solid phase which separates. Some experiments were made with gold amalgams in order to test the possibility of using this metal for reference. The solubility of gold in mercury at 20° was found from 3 determinations to be 0.00154, 0.00156, and 0.00156 g. of gold per g. of amalgam. From these results it was concluded that gold would make a good reference metal, since we desired a very dilute amalgam in order to change the chemical character of the mercury as little as possible. It was found, however, that gold was practically insoluble in magnesium amalgam, and this method was abandoned in favor of the method of directly analyzing the filtrate.

**Theory of the Method of Analyzing the Filtrate.**—Starting with an amalgam of known concentration, a known amount of liquid ammonia is introduced into the containing tube. Since we have established the fact that 6 mols of ammonia combine with 1 gram atom of magnesium we

<sup>19</sup> Kerp, *Z. anorg. Chem.*, 17, 284 (1898).

<sup>20</sup> Kerp, Böttger, Winter and Iggena, *ibid.*, 25, 1 (1900).

<sup>21</sup> C. van Eyk, *Proc. Acad. Sci.*, Amsterdam, 10, 859 (1902).

<sup>22</sup> A. van Bijlert, *Z. physik. Chem.*, 8, 343 (1891).

<sup>23</sup> Bancroft, *J. Phys. Chem.*, 6, 178 (1902).

<sup>24</sup> Van Heteren, *Z. anorg. Chem.*, 42, 129 (1904).

can calculate from the total amount of ammonia introduced the weight of magnesium that is removed from solution. This value must be corrected, however, for the solubility of the crystals in the residual amalgam and for the vapor pressure of the crystals which corresponds to the amount of ammonia not reacting. Using this corrected value for the amount of magnesium removed from the liquid phase we may indicate the number of gram atoms of mercury that are also removed from the liquid phase by letting  $x$  represent the number of gram atoms of mercury present in the crystal with 1 gram atom of magnesium and 6 mols of ammonia. The ratio of the remaining amount of mercury to magnesium in the liquid phase may now be equated to the ratio of magnesium found by direct analysis in the filtrate. The equation is written as follows,

$$\frac{W_1 - \left\{ \left[ \frac{1}{6} (N - P) - S.A \right] 200.6 x \right\}}{W'_1 - W'_2} = \frac{W_2}{W'_2}$$

where  $W_1$  is the weight of mercury in the original amalgam,  $N$  the number of mols of ammonia introduced,  $P$  the number of mols of ammonia that remain in the vapor phase,  $S$  the solubility of the crystals expressed as gram atoms of magnesium per gram of mercury,  $A$  the number of grams of mercury in the filtrate (liquid phase),  $W'$  the weight of magnesium in the original amalgam,  $W'_1$  the weight of magnesium removed in the crystals,  $W_2$  the weight of mercury in the filtrate,  $W'_2$  the weight of magnesium in the filtrate,  $\frac{1}{6}$  the ratio of gram atoms of magnesium to mols of ammonia and 200.6 is the atomic weight of mercury. The quantity in brackets  $\left\{ \left[ \frac{1}{6} (N - P) - S.A \right] 200.6 x \right\}$  represents the number of grams of mercury removed from the liquid phase as part of the crystals.

$W'_1$  is equal to  $\left\{ \frac{1}{6} (N - P) - S.A \right\} 24.32$  g. of magnesium, where 24.32 is the atomic weight of magnesium. In multiplying  $S$  by  $A$ , the number of grams of mercury in the filtrate, we are neglecting the weight of mercury present in the amalgam adhering to the crystals. However, since  $S$  is very small and the amount of amalgam adhering to the crystals is small, we are making only a small error and gaining simplicity in the equation.

**Method of Introducing a Known Weight of Ammonia.**—The amalgams were made by weighing out the magnesium and introducing the mercury from the Reservoir  $W$  (see Fig. 3) *in vacuo* by means of a calibrated pipet ( $P$ ) and a 3-way stopcock ( $S$ ), as described above. The volume of the containing tube ( $C$ ) up to Stopcock  $S$ , plus the connecting tubes to Stopcocks  $F$ ,  $R$ ,  $G$  and  $H$ , was determined by filling with dry ammonia gas, reading the pressure recorded on the gage ( $I$ ), and allowing the ammonia gas to expand into one of the expansion bulbs ( $B$  or  $E$ ), whose volumes were accurately known. From the new pressure recorded on the gage ( $I$ ) and the temperature, the volume was calculated. The volume of the containing tube was determined in the same manner.

Since we wished to filter these amalgams after the crystals had been formed it was necessary to condense into  $C$  only a limited amount of ammonia, excess of magnesium being used in all cases. The maximum amount of ammonia that could be used and still allow filtering was about 0.065 mol. for 200 g. of amalgam. Ammonia was condensed



into T through H where it was freed of traces of moisture with metallic sodium. Stopcock R was opened to the vacuum pump several times in order that any small amounts of hydrogen evolved in the drying process might be removed. The dry liquid ammonia in T was now allowed to expand into the containing tube, the connecting tubes, and one or both of the Bulbs B and E, depending on the amount that was desired. After reading the pressure on the gage (I) the ammonia gas was condensed into C by cooling in carbon dioxide and ether mixture until the desired pressure was shown on the gage. The containing tube was then sealed off at M and N under reduced pressure. From the initial and final pressures on the gage, the volumes of the connecting tubes, the Bulbs B and E, and the containing tube, with the temperature, the number of mols of ammonia introduced into C could be calculated. Since ammonia vapor deviates appreciably from a perfect gas under these conditions, all calculations were made using the Berthelot

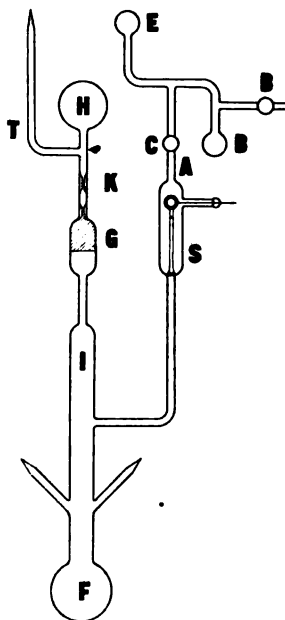


Fig. 5.

equation of state, which holds closely enough for ammonia vapor at these temperatures and pressures for our purposes. Corrections were made for the different heights of the mercury columns on the gage and for the lengths of tubing sealed off above M and N to the stopcocks.

**Method of Filtering the Amalgams.**—After the tubes had stood for several weeks and the absorption of ammonia was complete, 2 small bulbs were sealed to the sealed stopcock at A as shown in Fig. 5. After complete exhaustion through Stopcock B, Cock C was closed and dry ammonia condensed into Bulb D through B. Stopcock B was then closed and the sealed Stopcock S opened. The containing tube was then inverted, allowing the amalgam and crystals to run from Bulb F upon the filter (G), which was of glass wool packed tightly. Test experiments had shown that this sort of filter allows no crystals to run through with the liquid amalgam. Tube T was immersed in mercury to a sufficient depth so that no ammonia gas could escape except when the pressure in H, due to compression, was greater than the vapor pressure of the crystals. In this way there was no tendency for the crystals to decompose. Stopcock C was now opened partially so that the ammonia vapor from the liquid ammonia in E could

slowly force itself through the sealed stopcock and back of the crystals and amalgam. As the ammonia pressure in I gradually became greater the liquid amalgam was forced smoothly, drop by drop, into the receiving bulb (H). When the filtering was complete the highly compressed ammonia gas in I forced itself through the crystals and began to escape under the surface of the mercury. The receiving bulb was now sealed off at T and at K.

The filtrates were analyzed for magnesium by the method of Gooch and Austin;<sup>15</sup> the mercury was obtained by difference. A summary of results is given in Table.III below.

**Solubility Determinations.**—The solubility term enters into the ratio equation given above, and this value was next determined. Excess of liquid ammonia was used in all cases and small amounts of magnesium. Not over 0.2700 g. of magnesium for 200.00 g. of mercury could be used,

for otherwise the material became too viscous to filter. Using excess of liquid ammonia, all of the magnesium was removed from the amalgam except that due to the solubility of the crystals. The total concentration of the magnesium in the filtrate represents the solubility.

After absorption, the excess of liquid ammonia was allowed to escape and the amalgam filtered as described above. Three determinations gave 0.0061 g., 0.0057 g., and 0.0060 g. of magnesium for 100.000 g. of mercury. The mean of these values, 0.00593 g. of magnesium for 100.000 g. of mercury is chosen as representing the solubility of the crystals in the amalgam at room temperature (22.4°).

**Vapor-pressure Measurements.**—In order to calculate the number of mols of ammonia that reacted with the magnesium to form the crystals it was necessary to obtain the vapor pressures of the crystals at the temperature at which the amalgams were filtered. Knowing the vapor pressures and the volumes of the containing tubes, the number of mols of ammonia not reacting could be calculated. The number of mols of ammonia that entered the crystals was obtained by subtracting this value from the total number of mols of ammonia introduced into the tube. It was impossible to make vapor-pressure measurements of the crystals which we wished to analyze, for a certain amount of decomposition takes place as the pressures came to equilibrium. Consequently, amalgams were made of the same concentrations as those which were filtered and approximately the same amounts of ammonia introduced. After standing for 4 weeks the vapor pressures were determined, keeping the bulbs at 22.4° in a water thermostat, constant within 0.05°. The average temperature at which the amalgams were filtered was 22.4°, hence this temperature was chosen as the one at which the vapor pressures were measured. The equilibrium pressure was reached in about 12 hours. A table of results is given below.

TABLE III  
VAPOR-PRESSURE MEASUREMENTS  
(See Fig. 6, Curve C)  
All Measurements in Thermostat at 22.4°

Expt.	Magnesium G.	Mercury G.	Ammonia introduced Mols.	Vapor pressures cm. of Hg
1	0.4293	206.490	0.0606	175.2
2	0.4617	206.564	0.0627	171.7
3	0.5545	206.878	0.0544	166.2
4	0.5696	206.582	0.0518	165.9
5	0.5965	206.832	0.0633	164.8

The curve is plotted with concentrations of magnesium as abscissas and vapor pressures as ordinates. Using the vapor pressures and the volumes of the containing tubes in which the amalgams were filtered, the number of mols of ammonia remaining in the vapor phase is calculated

and substituted in the equation given on p. 15. A table summarizing all results is given below.

TABLE IV  
GRAM ATOMS OF MERCURY PRESENT

Determination	$W_1$	$W'_1$	$N$	$P$	$S, A$
1	206.490	0.4293	0.0610	0.00725	0.00026
2	206.564	0.4617	0.0624	0.00783	0.00020
3	206.582	0.5696	0.0519	0.00793	0.00020
4	206.832	0.5965	0.0636	0.00813	0.00016
5	206.686	0.6108	0.0586	0.00743	0.00020

	$\left\{ \frac{W'_1}{N-P} - S, A \right\}$	$24.32 W'_1 - W''_1$	$W_1$	$W'_2$	$x$
1	0.2116	0.2177	106.1872	0.1322	18.1
2	0.2163	0.2454	82.8769	0.1163	17.8
3	0.1734	0.3962	91.8776	0.2002	17.5
4	0.2209	0.3756	64.5923	0.1394	18.0
5	0.2025	0.4083	86.9291	0.2017	18.4

**Discussion of Results.**—The average value of  $x$ , as given in the foregoing table, is 17.96, which represents the number of gram atoms of mercury for each atom of magnesium in the solid phase. It appears, in con-

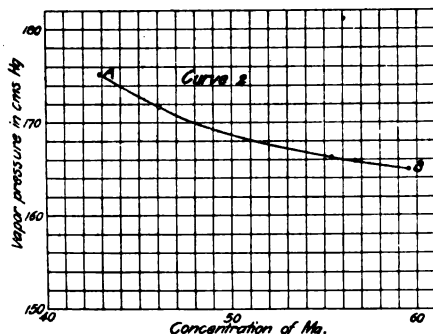


Fig. 6.

sideration of this rather large value for the amount of mercury in the solid phase and the small range of concentration covered in the analyses, that the compound magnesium hexammoniate forms a solid solution with the excess mercury of the amalgam. It is impossible to extend the measurements over wider ranges of concentrations than those given in Table IV, *i. e.*, between points A and B of Curve 2, for with larger amounts of magnesium than represented by B of Curve 2, and for larger amounts of ammonia than those given in Table IV, the entire amalgam becomes solid and cannot then be filtered. Thermal measurements are impracticable in this case on account of the very slow reaction in the system. The lack of a sharp melting point of the crystals is further evidence of the formation of solid solutions. It is to be expected that the formation of solid solutions would favor the formation of this molecular compound since its dissociation pressure is lowered thereby.

It is interesting to compare the values of  $W'_1 - W''_1$  with corresponding values of  $W'_2$  in the table. In each case  $W'_1 - W''_1$  is considerably larger, which indicates the amount of mother amalgam that wets the crystals,

even though they were subjected to a pressure of 6 to 7 atmospheres in the process of filtration by the pure liquid ammonia at room temperature.

### Summary.

A description is given of the general properties of a solid phase which separates from dilute magnesium amalgams when liquid ammonia is allowed to react with these amalgams.

Vapor-pressure measurements were made at  $0^{\circ}$  as ammonia vapor was removed from the system, thus decomposing the solid phase. From phase rule relationships it was concluded that two solid phases were present besides the vapor phase, one at least of which was variable in composition.

Experiments were undertaken to determine if the solid phase was variable in composition. A method is described for making pure amalgams and determining the ratio of magnesium to ammonia combined in the solid phase. It is shown that this ratio is 1 gram atom of magnesium to 6 mols of ammonia for amalgams of widely differing concentrations.

The solubility of magnesium in mercury at room temperature ( $22.4^{\circ}$ ) was determined, also the solubility of gold in pure mercury and in magnesium amalgams at  $22.4^{\circ}$ .

Various methods are discussed for analyzing the crystals for mercury of constitution, and a ratio equation developed to determine their constitution by analysis of the filtrate.

A method is described for making pure magnesium amalgams of known concentrations and introducing a known weight of pure liquid ammonia. The method of filtering the crystals from these mixtures is described in detail.

The solubility of the crystals in pure mercury was determined at  $22.4^{\circ}$ .

Vapor-pressure measurements were made of mixtures of exactly the same compositions as those which were filtered, and the results plotted.

Using a ratio equation containing terms that take into account the weight of magnesium and mercury in the original amalgam, the number of mols. of ammonia added, the solubility and vapor pressure of the crystals, and the analysis of the filtrate, calculations are made for the amount of mercury combined in the crystal. This value is found to be 18 gram atoms of mercury to 1 gram atom of magnesium and 6 mols of ammonia.

From the large value thus obtained for the amount of mercury combined it is concluded that solid solutions are formed by the molecular compound magnesium hexammoniate with the excess mercury present.

In conclusion it is a pleasure to acknowledge my thanks to the late Dr. William Argo, who suggested the problem and gave valuable assistance; also to Professor W. C. Bray for his helpful suggestions in interpreting many of the results.

BERKELEY, CALIFORNIA AND WASHINGTON, D. C.

[CONTRIBUTION FROM FIXED NITROGEN RESEARCH LABORATORY.<sup>1</sup>]

## A METHOD OF DETERMINING TRACES OF OXYGEN IN HYDROGEN.

BY ALFRED T. LARSON AND ERNEST C. WHITE.

Received August 22, 1921.

### Introduction.

In the synthesis of ammonia by the Haber Process a convenient and accurate method for estimating traces of oxygen in hydrogen-nitrogen mixtures is very desirable. None of the existing methods affords the degree of sensitivity and the rapidity of operation necessary to determine accurately the low concentrations to which this impurity must be limited.

One method which has been used for the estimation of oxygen consists in passing the gas over a contact mass which converts the oxygen into water; the water is then collected in an absorbent, usually phosphorus pentoxide, and weighed. In order to collect weighable quantities of water a very large volume of gas must be passed through the absorbent. For example, if the gas contains 0.001% of oxygen, 62 liters of the gas give only a milligram of water. Because of the difficulties involved in the complete absorption and the weighing of such small quantities of water, it is obvious that the method must be slow and inaccurate.

A colorimetric method has been developed which depends upon the conversion of colorless cuprous solutions into blue cupric solutions in the presence of oxygen. The intensity of this color change is made a measure of the oxygen content of the gas. This method has the advantage of being fairly rapid, but for very low concentrations of oxygen lacks the desired accuracy.

We undertook therefore the development of a rapid and accurate method of analysis for oxygen in hydrogen, where the concentration of oxygen might be as low as 0.001%. The success which had been met by Lamb and Larson<sup>2</sup> in the determination of low concentrations of carbon monoxide in air, suggested the possibility that this same principle at least could be applied to the estimation of oxygen in a large excess of hydrogen. In this method the combination of the trace of contained oxygen with the excess of hydrogen is catalyzed by platinum at 275–300°, and the temperature rise is measured by a thermocouple. The method is obviously not an absolute one; that is, the apparatus must be calibrated by the use of gas mixtures of known concentrations. This calibration of the apparatus proved, however, to be a very simple matter.

Since the temperature differences to be measured were very small, the needs of this work called for much closer regulation of the vapor bath

<sup>1</sup> Published by permission of the Secretary of Agriculture.

<sup>2</sup> Lamb and Larson. *THIS JOURNAL*, 41, 1908 (1919).

surrounding the platinum catalyst than had been found necessary in the work on the determination of carbon monoxide in air. That is, the accidental variations in the vapor bath might easily mask the temperature changes produced by the reaction on the platinum catalyst. The description of the apparatus and the discussion which follows will make evident the way in which the apparatus was designed so as to overcome these difficulties.

### Apparatus.

As shown in the accompanying diagram the apparatus consists essentially of a gas train, a platinum catalyst surrounded by an insulated vapor bath, a copper-constantan thermocouple, and a high sensitivity galvanometer.

A stream of purified hydrogen-nitrogen mixture (3:1) obtained by "cracking" ammonia was passed directly through the flowmeter C, or through the heated palladium-asbestos (350°) in B. Just ahead of the flowmeter was an adjustable regulator consisting of an outlet tube immersed in a movable column of liquid petrolatum. This outlet tube facilitated the close regulation of the gas flow. The meter was of the conventional capillary type, and found to be accurate within 0.5% for a flow of 500 cc. per minute.

At D there was joined to the train the outlet from an electrolytic cell E containing conc. potassium hydroxide solution. By suitably adjusting the resistance in F, the current from the storage battery G, as indicated by the milli-ammeter H, could be regulated to the value required for a given evolution of oxygen.

A 3-way cock J was provided so that the gas could be by-passed through the phosphorus pentoxide tube K before entering the catalyst tube. L was a wax-sealed ground glass connection, the tubing beyond this point being of Pyrex glass.

The gas entered the preheating coil M, which was made from about 3 meters of 4 mm. tubing, the dimensions of the coil being about 30 × 3 cm. At N (see enlargement at right) the gas entered the outer tube O, of 10 mm. diameter, passing downward to its lower end, then up through the inner tube P, which contained the platinized platinum gauze Q and the thermocouple junctions R and S. The "cold" junction R and its copper lead were insulated with a single piece of thin-walled capillary glass tubing shaped like the letter J. This insulation was found to be necessary in order to prevent premature catalysis on the surface of the copper wire at or near the "cold junction," an effect which might be sufficiently pronounced to generate an appreciable counter e. m. f. and even give a "negative" galvanometer deflection. The hot junction was imbedded near the top of the platinum catalyst. In order to diminish the Becquerel

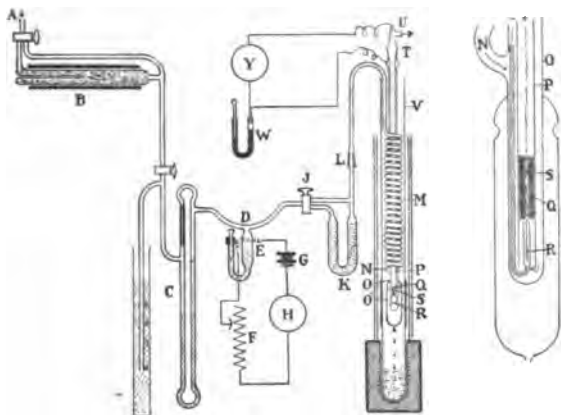


Fig. 1.

effect due to lack of homogeneity, the copper wire used was first subjected to careful annealing and subsequently handled in a manner to avoid excessive strains.

O' was a glass apron, sealed to O, and designed to safeguard the uniformity of temperature in that region, both by shedding the condensed liquid and by shielding the interior from other disturbances. Perforations near the top of this apron allowed free circulation of vapor, while the constricted aperture at the bottom prevented the entrance of superheated vapor.

The inner tube P was flared and ground to fit the mouth of the outer tube at T. This joint and the orifices admitting the copper wires were made air-tight with sealing wax. The gas emerged from the side arm U.

V was a Pyrex tube 6 × 70 cm. employed as a vapor bath. It was insulated with an air jacket formed between it and an outer tube wrapped with asbestos paper. The 10cm. length immediately surrounding the "vital" zone was closely wrapped with sheet metal. The bath was heated by an electric furnace to a temperature just sufficient to keep the condensation zone a few cm. below the top of the tube V. Diphenylamine, boiling at 305°, was found a convenient substance for the bath, but it undergoes gradual alteration and had to be renewed occasionally. Diphenyl was also used and found to disintegrate less rapidly, but unfortunately its boiling point, 255° is very close to the minimum temperature at which platinum will completely catalyze the combustion of hydrogen. We found it safer to employ diphenylamine.

Y was a Leeds and Northrup high-sensitivity galvanometer giving a deflection of 11.0 mm. per microvolt when no external resistance was used. It was mounted on a rigid support and encased in a wooden box with a small glass window, the box serving to maintain a fairly uniform temperature at the contact posts. When readings were to be taken, the thermo-electric circuit was closed by raising the mercury level in the tube W, in which were inserted the ends of the two wires. The ordinary knife switch could not be used at this point because of the uncertain contact potentials which it introduced. No trouble was experienced with this mercury contact switch.

### Calibration.

The problem of obtaining a low-concentration gas of known oxygen content for use in calibration presented some unforeseen difficulties, but the method finally adopted proved very satisfactory. A constant flow of 500 cc. (N. T. P.) of purified hydrogen-nitrogen mixture was maintained through the apparatus, and was found to produce a slight negative deflection of the galvanometer. This deflection was reasonably constant and reproducible, and was employed as a blank correction for subsequent

TABLE I  
CALIBRATION AT FLOW OF 500 CC./MIN.

Date	Current through electrolytic cell Milli-amperes	Oxygen concentra- tion %	Galvanometer (cm. scale)		
			Average reading	Average blank	Average deflection
May 6	2.12	0.00148	1.45	-2.30	3.75
	4.14	0.00288	5.60	-2.30	7.90
	6.27	0.00437	10.60	-2.30	12.90
	10.41	0.00725	20.70	-2.30	23.00
May 7	0.71	0.00049	-1.05	-2.25	1.20
	2.12	0.00148	1.55	-2.25	3.80
	3.14	0.00218	3.60	-2.25	5.85
May 10	10.41	0.00725	20.15	-2.85	23.00

readings. The calibration was then effected by passing through the electrolytic cell a succession of measured currents, allowing sufficient time at each setting for a uniform gas mixture to develop. Since each milli-ampere liberates  $82.9 \times 10^{-6}$  mg. of oxygen per second, an easy calculation gives the concentration resulting with a dilution of 500 cc. per minute. Readings of the galvanometer were then taken continuously for a period of 10 to 15 minutes, and were found to reach a very constant value within 5 minutes. These readings are given in Table I and are shown graphically in Fig. 2.

In the Table I, the average galvanometer reading represents the mean of ten or more observations at intervals of 30 seconds. Fluctuations from the average seldom exceeded 0.25 cm. Blanks on purified gas were taken frequently during the runs.

From the calibration curve it becomes a simple matter to determine the oxygen content of an oxygen-nitrogen-hydrogen mixture containing an unknown amount of oxygen. For example, on May 6, a gas which was known to contain 0.00582% oxygen was examined by this method. From the calibration curve the oxygen content was found to be 0.00585%;

likewise, on May 7, a gas containing 0.00077% oxygen showed 0.00079% by this method. From these results it would seem that the apparatus is satisfactory down to about 0.00003% of oxygen. In other words, in the estimation of a gas containing 0.001% oxygen the error would be about 3%.

In this connection it was thought to be of interest to compare the observed galvanometer deflections with those that would be expected if the thermal system were 100% efficient, *i. e.*, if there were no heat losses to the surroundings of the combustion zone. Taking the average molar heat of the gas mixture at  $305^\circ$  as 7.034, and

the heat liberated from  $5 \times 10^{-6}$  mols. of oxygen as 5.836 calories, the temperature rise of a 0.005% gas would be  $0.83^\circ$ . Assuming the thermoelectric power of the copper-constantan couple to be 60.0 microvolts per degree the e.m.f. would be 49.8 microvolts, and should produce a

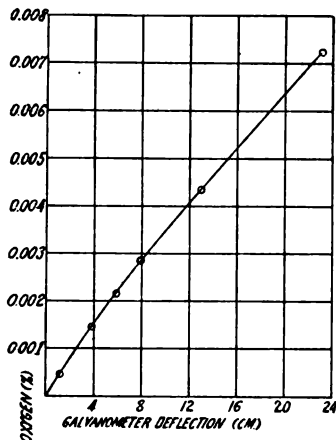


Fig. 2.

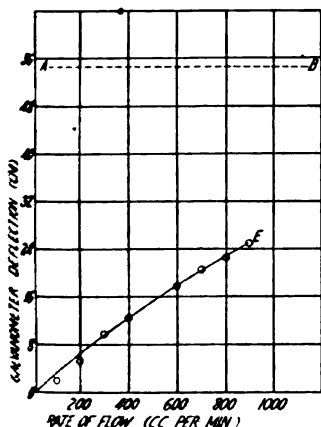


Fig. 3.



deflection of 54.8 cm. The experimental calibration curve gives 15.1 cm. as the actual deflection produced by a gas of this concentration at 500 cc. per minute, or about 28% of the calculated value.

It is evident therefore that the heat losses to the surroundings are quite considerable. The relation of rate of flow to these heat losses was determined by a series of experiments the results of which are recorded in Table II and shown graphically in Fig. 3.

TABLE II  
EFFECT OF RATE OF FLOW ON E. M. F. PRODUCED  
0.005% Oxygen

Rate of flow Cc./min.	Current through electrolytic cell Milli-amperes	Galvanometer (cm. scale)		Average deflection
		Average reading	Average blank	
100	1.44	-1.70	-3.80	2.10
200	2.87	1.90	-3.35	5.25
300	4.31	6.70	-3.20	9.90
400	5.75	9.70	-2.90	12.60
600	8.62	15.95	-1.70	17.65
700	10.06	19.10	-1.40	20.50
800	11.50	21.80	-0.70	22.50
900	12.93	24.60	-0.30	24.90

If there were no heat losses the galvanometer deflection would be a constant represented by the line A-B. It is evident from the manner in which the observed values are approaching this theoretical value A-B that a comparatively high flow must be reached before the variations in the rate would produce negligible effects upon the galvanometer deflections.

The thermal efficiency of the apparatus could no doubt be greatly improved by vacuum jacketing the catalyst, for example. If this were successful, the galvanometer readings obtained on a given gas would be less affected by variations in the rate of flow through the apparatus.

Or we might have increased the capacity of the preheating coils so that much higher rates of flow could have been employed. Probably with a flow of 2000 cc. per minute the effect of variations in the rate of flow would have been smaller. Since the exact regulation of the gas flow was a comparatively simple matter, we elected to calibrate the apparatus for a definite rate of flow. Even with the very great heat losses, it still had sufficient accuracy to make it reliable in determining the oxygen content of a nitrogen-hydrogen mixture.

Certain precautions were found necessary in the operation of this apparatus. First, the vapor bath was never heated until the apparatus had been thoroughly swept out with oxygen-free gas. While a large quantity of oxygen might not produce an explosion, still there is danger that the temperature of the catalyst would be raised to such an extent that its activity would be considerably diminished if not wholly destroyed. Sec-

ond, the galvanometer was always disconnected or short-circuited until the bath had reached the proper temperature.

It was found advisable, when extreme accuracy was desired, to make frequent observations of the "blank" correction that had to be applied to the galvanometer readings. Prolonged use of diphenylamine in the bath results in superheating of the lower or "cold" junction and a consequent negative galvanometer deflection of increasing magnitude. Other minor causes introduce slight variations. The method of making the "blank" observation consisted simply in by-passing the gas stream through the heated palladium-asbestos and allowing several minutes for the train to be swept with the purified gas.

Poisoning of the platinum catalyst may result from the presence of halogens or sulfur compounds. If the gas contains such impurities they must be completely removed before the gas is permitted to reach the catalyst. Extreme poisoning generally necessitates removing the platinum and reactivating it by purifying and replating.

The apparatus described in this article was designed to operate on a gas which did not contain oxygen in excess of 0.01%. Higher concentrations of oxygen would require the introduction of an external resistance in the galvanometer circuit or the use of a less sensitive instrument. However, if the apparatus be used to examine a gas whose oxygen content is much in excess of 0.1%, say, 1 or 2%, the activity of the platinum catalyst may be lowered considerably and much of the oxygen passed through without combining. By operating the whole catalyst at a higher temperature, say 400–450°, this difficulty would no doubt be obviated.

### Summary.

1. The necessity for an accurate and rapid method for analysis of oxygen in nitrogen-hydrogen mixtures has been explained.

2. A thermometric method which is both rapid and accurate has been described. In this method the gas mixture is passed through a platinized platinum catalyst where the temperature rise is measured by a thermo-element. Deflections of a galvanometer attached to this thermo-element are made the measure of the oxygen content of the gas mixture. Concentrations of oxygen as low as 0.001% may easily be determined, the error being about 3%.

3. A device for introducing a definite quantity of oxygen into the oxygen-free gas has been described. This facilitates calibration and checking of the apparatus. A specimen calibration curve has been included.

4. Attention has been called to the details in construction and the manipulation of the apparatus which will insure its successful operation.

WASHINGTON, D. C.

[CONTRIBUTION FROM THE KENT CHEMICAL LABORATORY OF THE UNIVERSITY OF CHICAGO.]

## A CONTINUOUS-READING ELECTROTITRATION APPARATUS.

By KENNETH H. GOODE.

Received August 22, 1921.

The simplest possible apparatus for electrometric titration, from a theoretical standpoint, would be a sensitive voltmeter connected between a calomel electrode and a hydrogen electrode. In practice, however, an ordinary voltmeter cannot be used, because the instrument would consume current enough from the cell to discharge the hydrogen electrode, and render it inoperative. For this reason all types of apparatus hitherto in use have depended upon balancing the unknown e.m.f. of the cell being used against a variable known e.m.f. produced by a potentiometer system, the balance being determined by a "null-point" galvanometer. With this type of apparatus a

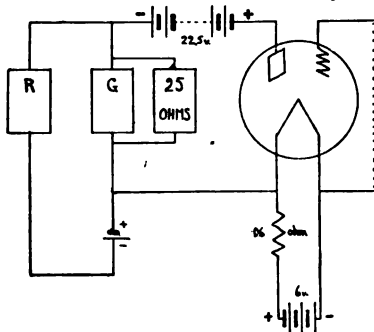


Fig. 1.—Diagram of original circuit.

balance of potentials must be made before each reading of the voltage, and there is considerable uncertainty in the readings when the potential of the cell is rapidly changing. The investigation described in this paper has shown that the 3-electrode vacuum valve ("audion") presents almost the ideal case of a "voltmeter" which draws no current from the source to be measured, and can therefore be employed as a continuous-reading instrument for determining the concentration of the hydrogen ion.

The 3-electrode valve consists of a highly exhausted glass bulb containing an incandescent filament surrounded by a grid of fine wire, which is itself surrounded by a metallic plate. A high voltage battery of 20 to 100 volts connected between the plate and the filament produces a current through the "plate circuit," whose magnitude is a function of the potential of the grid. This plate current, ( $I_p$ ), may be considered as the sum of a constant current, ( $I_0$ ), which is independent of the grid potential, and a current ( $I_p - I_0$ ) which is nearly a linear function of the grid potential. In order to measure ( $I_p - I_0$ ) it was found necessary to balance the

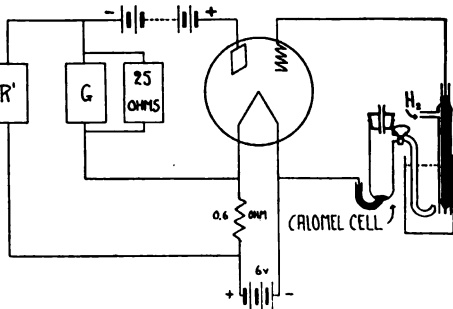


Fig. 2.—Diagram of improved circuit.

current  $I_0$  with an equal current in the opposite direction. The remaining current is measured with a galvanometer or micro-ammeter, which may be calibrated to read directly in volts, or in Sørensen units ( $P_H$ ). With the proper connections, the current in the grid circuit, through the titration cell, is negligible, so that no circuit-breaking key is required, and the current ( $I_p - I_0$ ) indicates at each moment the potential of the hydrogen electrode.

The vacuum tube used was a "Radiotron," type UV 201, which was lighted by means of a 6-volt storage battery. The filament current was adjusted at 1.06 amperes by the introduction of a resistance of about 0.6 ohms. Under these conditions the potential of the battery was 6.1 volts, while that across the terminals of the resistance was 0.6 volts. The plate battery was a 22.5-volt unit, giving a steady plate current ( $I_0$ ) of 0.00045 amperes. It

was at first thought that this steady current could be balanced by the torsion of the galvanometer suspension, but this was found impracticable because of a steady shift of the zero point. It was found possible, however, to balance the steady current by an equal and opposite current produced by a dry-cell acting through about 3000 ohms or resistance,  $R$  (Fig. 1). The circuits were later simplified, and a more steady zero point obtained by replacing this battery by the potential difference at the terminals

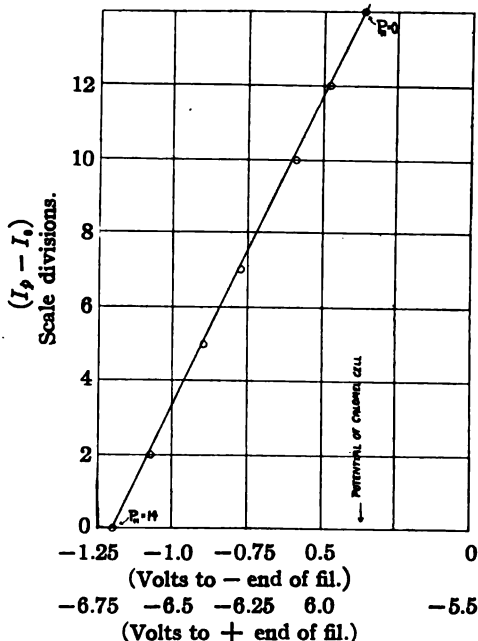


Fig. 3.—Variation of  $(I_p - I_0)$  with potential of grid.

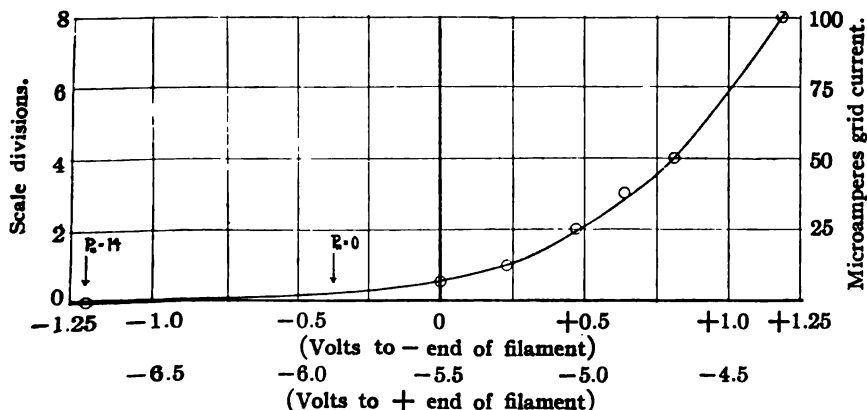


Fig. 4.—Effect of potential on grid current.

of the filament resistance, acting through an adjustable resistance,  $R'$ , of about 1300 ohms (Fig. 2).

In order to obtain a steady zero point, the filament current must be maintained at a constant value, which is possible only by protecting the filament resistance and its connecting wires from slight changes of temperature. With this precaution a perfectly steady and reliable zero point is assured.

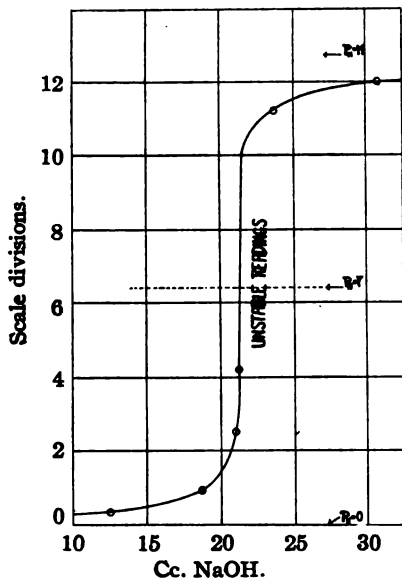


Fig. 5.—Titration of HCl.

of  $I_p - I_0$  in scale divisions. Although necessarily situated on a curve, the points lie within 1% of the straight line, representing a linear relation between  $I_p - I_0$  and the corresponding Sørensen value.

The current in the grid circuit of an audion depends upon the potential of the grid, measured with respect to the positive terminal of the filament; and at potentials near zero, (*i. e.*, with the titration cell connected between the grid and the *positive* end of the filament), the current is so great

For measuring the current,  $I_p - I_0$ , a D'Arsonval galvanometer, G (Figs. 1 and 2), having a sensitivity of  $0.62 \times 10^{-6}$  amperes per scale division<sup>1</sup> was employed. By using a shunt of 25 ohms, the sensitivity was reduced to  $10.1 \times 10^{-6}$  amperes per scale division, which corresponded very closely to one Sørensen unit ( $P_H$ ) for each scale division under the conditions in which it was finally used. Fig. 3 shows the calibration curve under these conditions, the abscissas being the potentials of the grid in volts, and the ordinates the values

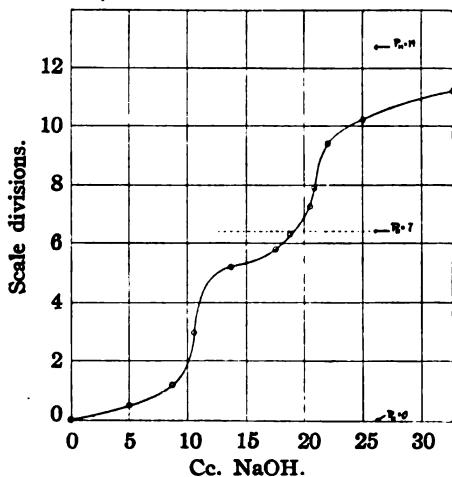


Fig. 6.—Titration of  $H_3PO_4$ .

<sup>1</sup> Deflections were observed by means of a telescope and scale, both located about 40 cm. from the galvanometer mirror, the scale divisions being each 1 cm. in length. The apparent angular displacement of the scale per micro-ampere, with the 25-ohm shunt, would then be  $0^\circ 8' 36''$ , or 0.0025 radians.

as to discharge the hydrogen electrode immediately. When the grid is given a negative potential, however, the current decreases, becoming zero at about  $-7$  volts. Fig. 4 indicates this effect, the ordinates being in this case scale divisions of a "Cenco" null-point galvanometer (1 scale division  $= 12 \times 10^{-6}$  amps.), while the abscissas are, as before, the potential of the grid in volts. Potentials near  $-5.5$  volts are conveniently obtained by connecting the titration cell between the grid and the *negative* end of the filament. By connecting the hydrogen electrode to the grid and the calomel electrode to the filament, potentials between  $-5.8$  and  $-6.7$  volts are obtained, within which range the grid current is entirely negligible.

Typical titration curves obtained with this arrangement are shown in Figs. 5 and 6. In these cases, and for all titrations, the terminals of the galvanometer were reversed and the resistance  $R'$  adjusted at such a value that the scale-reading was zero when the Sørensen value was zero. By a careful adjustment of the shunt resistance, the scale divisions will now directly indicate the Sørensen values in the titration cell.<sup>2</sup> Some difficulty was experienced in getting constant readings in regions of the curves where the Sørensen value changes abruptly, because the stirring necessary to produce a homogeneous solution resulted in a momentary decrease in the potential of the hydrogen electrode of about  $0.02$  volts. For this reason it was found necessary to stop stirring about 2 seconds before each reading was taken. With a constant stirring apparatus it might be possible to allow for this effect.

The sensitivity of the apparatus described in this paper is of the order of  $0.1$  Sørensen unit, or  $0.006$  volts. By merely employing a galvanometer scale capable of being read to  $0.01$  scale division (defined as before), the sensitivity might be increased tenfold, but unless the effect of stirring mentioned above is nullified, further improvement in this direction would seem useless.

The writer wishes to express his appreciation of the advice of Dr. Gerald L. Wendt in connection with this work.

CHICAGO, ILLINOIS.

<sup>2</sup> In the titrations of Figs. 5 and 6, however, adjustment could only be made to the nearest ohm (25 ohms), and 14 Sørensen units are here represented by 12.8 scale divisions.

[CONTRIBUTION FROM THE GEOPHYSICAL LABORATORY OF THE CARNEGIE INSTITUTION OF WASHINGTON.]

## THE CRYSTAL STRUCTURES OF THE CUPROUS HALIDES.

BY RALPH W. G. WYCKOFF AND EUGEN POSNJAK.

Received September 1, 1921.

### Introduction.

This determination of crystal structure will outline the manner of application of the general method of study based upon the results of the theory of space groups<sup>1</sup> to cubic compounds of the type  $RX$  (where  $R$  and  $X$  are atoms of the same valence) when all of the diffraction data are furnished by a study of the powder photograph from the crystal under investigation.

In order to arrive at a definite structure for such a crystal it is necessary to make the assumption that its structure is simple, since the present lack of precise knowledge concerning the laws which govern the scattering of X-rays by different atoms makes it impossible to eliminate with certainty the one or more complicated structures which can be equally well brought into qualitative agreement with the observed diffraction data from any crystal. Because no crystals of this type have as yet been found for which it is necessary to assign a structure containing more than 4 molecules within the unit cell in order to arrive at a qualitative agreement with the experimental results, discussion will be here limited to possible structures having not more than 4 molecules in the unit.

**The Crystalline Material.**—The cuprous halides were prepared in the ordinary fashion, the chloride and bromide by the reduction of the corresponding cupric salts with sulfur dioxide, the iodide by the reaction between a cupric salt and potassium iodide. The copper iodide prepared in this fashion was sufficiently fine grained so that it could be immediately formed into a suitable film with collodion. Some difficulty was experienced in preparing films of the other two salts because of the readiness with which they undergo oxidation. They were finally obtained in suitable films by the use of molten Canada balsam.

Several unsuccessful attempts were made to grow crystals of the iodide of sufficient size so that reflection photographs from a known crystal face might be made to give the number of molecules to be associated with the unit cube. Several large and externally well-formed dodecahedrons (more than 0.5 cm. in diameter) of the cuprous chloride<sup>2</sup> were available for study. Attempts to prepare Laue photographs with sections from several of these specimens invariably led to photographs showing only a few scattered and much distorted spots. Several efforts to obtain reflection spectra by the usual rotating crystal method from both the cube and the dodecahedral faces and using both the L-radiation of tungsten and the K-radiation of molybdenum were likewise failures.

<sup>1</sup> Niggli, "Geometrische Krystallographie des Discontinuums," Gebrüder Borntraeger, Berlin, 1919.

Ralph W. G. Wyckoff, *Am. J. Sci.*, 1, 138 (1921), etc.

<sup>2</sup> These crystals were provided through the courtesy of H. E. Merwin of this laboratory.

The reflections from the powder films that were made in the way already outlined were, however, satisfactory. The powder spectrograph was the same as that previously used by one of us<sup>3</sup> and resembles, though it is of smaller size and does not possess so many arrangements for the shielding from secondary radiation, a spectrograph recently described.<sup>4</sup> Satisfactory results were achieved by using simply a zirconium oxide filter which was in contact with and covered the entire face of the photographic film. This screen thus served the double purpose of rendering the primary rays monochromatic and of absorbing secondary radiation from both the spectrometer and the crystalline film. Such a filter in contact with the photographic plate is a necessity if any diffraction is to be recorded in the case of the cuprous bromide because of the very large amount of secondary radiation emitted, for the most part, by the bromine of the salt.

Because of discrepancies in the recorded values redeterminations of the *density* of cuprous chloride and cuprous iodide were made by a pycnometer method.<sup>5</sup> The density of the chloride at 30° against water at 4° was thus found to be 4.136, for the iodide 5.667. The only recorded value of the bromide,<sup>6</sup>  $\rho = 4.72$  is in good agreement with the diffraction measurements.

The *symmetry* of the crystals of the cuprous halides is described as that of the tetrahedral class (hemimorphic hemihedry) of the cubic system. The arrangement of the atoms in the unit cells of these crystals must therefore be defined by special cases of one of the space groups,  $T_d^1 - T_d^7$ , having tetrahedral symmetry.

### The Possible Arrangements of the Atoms in the Unit Cells.

*One Chemical Molecule within the Unit.*—There is but one way of placing a single molecule of a compound  $RX$  within the unit so that the arrangement possesses cubic symmetry. These two special cases having a single equivalent position within the unit are special cases of the space group  $T_d^1$ . On the basis of the arrangement of its equivalent positions (or atomic positions) the symmetry of this possible grouping is that of the holohedry of the cubic system. Any lower degree of symmetry, such as is evident in the case of crystals of the cuprous halides, would be attributed to some lack of symmetry in the atoms themselves. This possible structure<sup>7</sup> for the crystals under investigation is as follows.

<sup>3</sup> Wyckoff, *Am. J. Sci.*, 2, 244 (1921).

<sup>4</sup> Hull, *Phys. Rev.*, [2] 17, 571 (1921).

<sup>5</sup> Johnston and Adams, *THIS JOURNAL*, 34, 566 (1912).

<sup>6</sup> Groth, "Chemische Krystallographie," Wilhelm Engelmann, Leipzig, 1906, Vol. 1, p. 199.

<sup>7</sup> The results in this paper dealing with all of the possible arrangements for the atoms in these crystals are based upon a complete analytical expression of the results of the theory of space groups prepared by one of the present writers but as yet unpublished.



Cu: 000.

X:  $\frac{1}{2}\frac{1}{2}\frac{1}{2}$ .

*Two Molecules within the Unit Cell.*—There is no possible way of arranging 2 molecules of a compound of the type RX within a unit cell so that the resulting structure will exhibit cubic symmetry.

*Three Molecules within the Unit Cell.*—But one way of placing 3 molecules of a compound RX within a unit cube is possible. This arrangement, also a special case of the space group  $T_d^1$ , is as follows.

(3a) Cu:  $\frac{1}{2}\frac{1}{2}0$ ;  $\frac{1}{2}0\frac{1}{2}$ ;  $0\frac{1}{2}\frac{1}{2}$ .

X:  $00\frac{1}{2}$ ;  $0\frac{1}{2}0$ ;  $\frac{1}{2}00$ .

In this arrangement again a degree of symmetry lower than that of the holohedry of the cubic system must be accounted for by some dissymmetry in the shape of the atomic fields of force.

*Four Molecules within the Unit Cell.*—Two space groups exhibiting tetrahedral symmetry have special cases with 4 equivalent positions in the unit cell. The possible structures derived from one of these,  $T_d^2$ , are

(4a) Cu: 000;  $\frac{1}{2}\frac{1}{2}0$ ;  $\frac{1}{2}0\frac{1}{2}$ ;  $0\frac{1}{2}\frac{1}{2}$ .

X:  $\frac{1}{2}\frac{1}{2}\frac{1}{2}$ ;  $00\frac{1}{2}$ ;  $0\frac{1}{2}0$ ;  $\frac{1}{2}00$ .

This, the "sodium chloride arrangement," has in the grouping of its atoms holohedral symmetry.

(4b) Cu: 000;  $\frac{1}{2}\frac{1}{2}0$ ;  $\frac{1}{2}0\frac{1}{2}$ ;  $0\frac{1}{2}\frac{1}{2}$ .

X:  $\frac{1}{4}\frac{1}{4}\frac{1}{4}$ ;  $\frac{1}{4}\frac{3}{4}\frac{3}{4}$ ;  $\frac{3}{4}\frac{1}{4}\frac{3}{4}$ ;  $\frac{3}{4}\frac{3}{4}\frac{1}{4}$ .

The symmetry of the arrangement of the atoms in this, the "zinc sulfide structure," is tetrahedral.

The arrangement of the atoms in the third of the possible structures<sup>9</sup> containing four molecules in the unit also gives tetrahedral symmetry. This structure is derived from the space group  $T_d^1$ . It is as follows:

(4c) Cu: uuu; uūū; ūuū; ūūu.

X: vvv; vūv; vūv; vūv

The values of the coördinates u and v can lie anywhere between zero and unity.

### The Choice of the Correct Structures.

Using the customary expression<sup>9</sup> for the calculation of the intensity of reflection from any arrangement of atoms, and taking A as the sum-

<sup>9</sup> If as is conceivable, though not probable perhaps, in the light of the existing crystallographic studies of these crystals, their symmetry is really tetartohedral, then one more structure which likewise contains four molecules within the unit cube is possible. This grouping, which is isomorphous with the space group  $T^1$ , is as follows:

(4d) Cu: uuu;  $u+\frac{1}{2}, \frac{1}{2}-u, \bar{u}$ ;  $\bar{u}, u+\frac{1}{2}, \frac{1}{2}-u$ ;  $\frac{1}{2}-u, \bar{u}, u+\frac{1}{2}$ .

X: vvv;  $v+\frac{1}{2}, \frac{1}{2}-v, \bar{v}$ ;  $\bar{v}, v+\frac{1}{2}, \frac{1}{2}-v$ ;  $\frac{1}{2}-v, \bar{v}, v+\frac{1}{2}$ .

A discussion of this possible structure in relation to the X-ray diffraction data will be given in a foot-note at a later point.

<sup>9</sup> Wyckoff, *Am. J. Sci.*, 50, 317 (1920).

mation of its cosine terms and B as the summation of the corresponding sine terms, the diffraction effects to be expected from copper and halogen atoms placed in each of these possible groupings can be readily calculated. They are for

**Arrangement (1a):**

When the indices of the reflecting plane are *two odd* and *one even*  $A = \bar{R} + \bar{X}$  for all values of  $n$ , where  $\bar{R}$  and  $\bar{X}$ , the scattering powers of the atoms of R and of X, are to be taken as roughly proportional to the atomic numbers and where  $n$  is the order of the reflection.

For indices *two even* and *one odd*, or *all odd*,  $A = \bar{R} - \bar{X}$  when  $n$  is odd,  $A = \bar{R} + \bar{X}$  when  $n$  is even. In all cases  $B = 0$ .

**Arrangement (3a):**

For indices *two odd* and *one even*,  $A = \bar{R} + \bar{X}$  when  $n$  is odd,  $A = 3(\bar{R} + \bar{X})$  when  $n$  is even. For indices *two even* and *one odd*,  $A = \bar{R} - \bar{X}$  when  $n$  is odd,  $A = 3(\bar{R} + \bar{X})$  when  $n$  is even. For indices *all odd*  $A = 3(\bar{R} - \bar{X})$  when  $n$  is odd,  $A = 3(\bar{R} + \bar{X})$  when  $n$  is even. In all cases  $B = 0$ .

**Arrangement (4a):**

For indices *two even* and *one odd*, or *two odd* and *one even*,  $A = 0$  when  $n$  is odd,  $A = 4(\bar{R} + \bar{X})$  when  $n$  is even. For indices *all odd*,  $A = 4(\bar{R} - \bar{X})$  when  $n$  is odd,  $A = 4(\bar{R} + \bar{X})$  when  $n$  is even. In all cases  $B = 0$ .

**Arrangement (4b):**

For indices *two even* and *one odd*,  $A = 0$  when  $n$  is odd,  $A = 4(\bar{R} \pm \bar{X})$  when  $n$  is even,  $+$  when  $n = 4, 8, \dots$ ,  $-$  when  $n = 2, 6, \dots$ . For indices *two odd* and *one even*,  $A = 0$  when  $n$  is odd,  $A = 4(\bar{R} + \bar{X})$  when  $n$  is even. In both of these cases  $B = 0$ . For indices *all odd*,  $A = 4\bar{R}$ ,  $\bar{B} = 4\bar{X}$  when  $n$  is odd,  $A = 4(\bar{R} \pm \bar{X})$  when  $n$  is even,  $+$  when  $n = 4, 8, \dots$ ,  $-$  when  $n = 2, 6, \dots$ ,  $B = 0$ .

**Arrangement (4c):**

$A = R[\cos 2\pi nu(h+k+1) + \cos 2\pi nu(h-k-1) + \cos 2\pi nu(k-h-1) + \cos 2\pi nu(1-h-k)] + \bar{X}$  [a similar term in  $v$ ].  $B =$  a sine term similar to the cosine term.

From these values of A and B the approximate intensity of reflection ( $I'$ ) from any plane  $hkl$  can be calculated for each of these arrangements through the use of the customary expression

$$I' \propto (d/n)^2 (A^2 + B^2)$$

the spacing  $d_{hkl}$  of any plane being obtained as usual from the relation

$$d_{hkl} = \frac{d_{100}}{\sqrt{h^2 + k^2 + l^2}}.$$

The intensity ( $I$ ) of a line in a powder photograph, the product of this  $I'$  into the number of planes ( $s$ ) in the crystal form to which the plane  $hkl$  is assigned, has thus been written

$$I_{hkl} \propto \frac{1}{(h^2 + k^2 + l^2)n^2} \times (A^2 + B^2) \times s$$

$d_{100}$  being written as unity. The constants of the spectrometer being known from a standardization with sodium chloride, it is a simple matter to derive from the equation  $d_{100}^3 = mM/\rho$  (where  $m$  = the number of molecules in the unit cube,  $M$  = the mass of one molecule of the salt and  $\rho$  = its density) the positions upon a spectrogram of the reflections from any plane of atoms for each of the possible structures. The carrying out of these two calculations, one of the intensity, the other of the positions of the reflections from all atomic planes, furnishes the manner of completely predicting the diffraction effects that would be obtained from the atoms of the substance under investigation arranged according to each of the possible crystal structures.

The intensities of reflection and the positions of the four strongest spectrum lines<sup>10</sup> thus calculated for each of the possible arrangements, except (4c), and for each of the salts under investigation are given in Tables I–IV. The observed positions of the spectrum lines and an estimate of their relative intensities are given for these crystals in Table V. Because of the uncertain character of the assumed values of the scattering powers of the different atoms and the approximate nature of the assumption that  $I \propto (d/n)^2$ , no more than a qualitative agreement is to be expected between the observed estimations of intensity and those calculated for the correct structures. It will be observed that of these various possibilities the only one which presents any agreement with observation is grouping (4b), the “zinc sulfide structure.” Furthermore it will be seen that the qualitative agreement in this case is good.<sup>11</sup> This leaves no doubt but that the correct structure for these cuprous halides is in each case either precisely the “zinc sulfide arrangement” or a close approach to it. A consideration of the other possible grouping, (4c), shows that it is not possible to assign such values to  $u$  and  $v$  that the resulting structure is an approach to (4b). It can then be definitely concluded that if their structures are simple ones and if their symmetry is really that of the tetrahedral class of the cubic system,<sup>12</sup> the crystal structures of cuprous chloride, cuprous bromide and cuprous iodide are in each case given by the “zinc sulfide arrangement.” The lengths of the sides

<sup>10</sup> In this instance no more lines are necessary to establish the structures.

<sup>11</sup> It is known from the experimentally established “normal decline” of intensity with spacing that this decline is at a rate faster than the square, as here assumed. All of the discrepancies between the calculated and the estimated intensities both in the case of those lines which are discussed and for other lines observed in the spectra but not recorded are found to be in accord with this fact.

<sup>12</sup> If the structure were tetartohedral, then grouping (4d) becomes a possibility (see Ref. 11). If in this grouping  $u = 0$  and  $v = 1/4$  the structure that results is identical with (4b). It is evident that qualitative agreement with experiment would also be ensured for values of  $u$  close to but not exactly equal to 0 and for values of  $v$  close to  $1/4$ .

of the unit cube, as calculated from the three strongest lines in each spectrum are

	A. U.
Cuprous chloride.....	5.49
Cuprous bromide.....	5.82
Cuprous iodide.....	6.10

TABLE I  
ARRANGEMENT (1a)

Plane	$n$	Calculated Spacings			Calculated Intensity		
		CuCl	CuBr	CuI	CuCl	CuBr	CuI
110	(1)	2.40	2.60	2.69	12.670	24.420	40.000
112	(1)	1.39	1.50	1.55	8.480	16.350	26.800
132	(1)	0.91	0.98	1.02	7.270	15.090	22.900
130	(1)	1.07	1.16	1.20	5.090	9.830	16.100

TABLE II  
ARRANGEMENT (3a)

Plane	$n$	Calculated Spacings			Calculated Intensity		
		CuCl	CuBr	CuI	CuCl	CuBr	CuI
100	(2)	2.45	2.65	2.74	28.600	55.300	90.800
110	(2)	1.73	1.87	1.94	28.300	55.000	90.200
120	(2)	1.09	1.18	1.22	22.700	43.900	72.000
112	(2)	1.00	1.08	1.12	19.000	36.700	60.250

TABLE III  
ARRANGEMENT (4a)

Plane	$n$	Calculated Spacings			Calculated Intensity		
		CuCl	CuBr	CuI	CuCl	CuBr	CuI
100	(2)	2.70	2.92	3.02	50.700	98.000	161.300
110	(2)	1.90	2.06	2.13	50.300	97.300	160.100
120	(2)	1.20	1.30	1.35	40.300	77.900	128.000
112	(2)	1.10	1.19	1.23	33.600	65.200	107.200

TABLE IV  
ARRANGEMENT (4b)

Plane	$n$	Calculated Spacings			Calculated Intensity		
		CuCl	CuBr	CuI	CuCl	CuBr	CuI
110	(2)	1.90	2.06	2.13	50.500	98.000	160.000
111	(1)	3.12	3.37	3.49	47.900	88.000	146.500
113	(1)	1.62	1.76	1.82	39.300	72.000	119.500
112	(2)	1.10	1.19	1.23	33.750	65.300	107.000
133	(1)	1.23	1.31	1.38	22.700	41.500	69.200 <sup>13</sup>

<sup>13</sup> Though the calculated intensity of this line is less than that of two others (not given), it is more intense upon the photographs than even (112). This, however, is not unexpected because of its greater spacing. See Ref. 11.

TABLE V  
OBSERVED VALUES

Observed Spacings			Estimated Intensity (10 = the strongest line)		
CuCl <sup>14</sup>	CuBr	CuI	CuCl	CuBr	CuI
3.18	3.37	3.52	10	10	10
1.93	2.04	2.15	8	8	9
1.65	1.75	1.84	7	6	8
1.26	1.31	1.38	0.3	2	2
1.14	1.18	1.24	0.1	1	1

### The Chemical Significance of these Crystal Structures.

It has previously been pointed out<sup>15</sup> that with compounds of a certain type (the valence compounds, in which the chemical bonds are electrons shared by two atoms) there might be such a connection between the positions of the atoms and their chemical valence as would enable the prediction of the manner of combination of the atoms of a compound from the arrangement of its atoms. It was also shown that all of the structures thus far studied with the X-rays were in agreement with this idea. A "zinc sulfide arrangement" of the atoms of a compound of the type  $RX$ , where both  $R$  and  $X$  are monovalent atoms, is not to be anticipated, however, upon these simple grounds. As a consequence of this study of the cuprous halides, then, it will evidently be necessary to abandon these simple considerations and, when attempting to correlate crystal structure and the nature of chemical combination, to view such factors as the shapes and sizes of atoms as important in determining the arrangement of the atoms in crystals.

### Summary.

Cuprous chloride, cuprous bromide and cuprous iodide all have the "zinc sulfide arrangement" of their atoms in crystals. The lengths of the sides of the unit cubes in the three cases are 5.49 A. u., 5.82 A. u. and 6.10 A. u.

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<sup>14</sup> These values are uniformly higher than the calculated spacings so that there can be no doubt that the new determination of density is somewhat in error. Its value, calculated from the observed spacings, becomes = 3.93.

<sup>15</sup> Wyckoff, *J. Wash. Acad. Sci.*, 9, 565 (1919); *J. Franklin Inst.*, 191, 199 (1921).

[CONTRIBUTION FROM THE KENT CHEMICAL LABORATORY OF THE UNIVERSITY OF CHICAGO.]

THE SEPARATION OF ISOTOPES. THEORY OF RESOLUTION OF ISOTOPIC MIXTURES BY DIFFUSION AND SIMILAR PROCESSES. EXPERIMENTAL SEPARATION OF MERCURY BY EVAPORATION IN A VACUUM.

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Introduction.

In January, 1920, Harkins and Broeker obtained by the method of diffusion a separation of the isotopes of chlorine amounting to a difference of density of 1.55 parts per thousand.<sup>1</sup> About 6 months later Brönsted and von Hevesy reported a much smaller resolution of the isotopes of mercury, amounting to about 50 parts per million difference in density, obtained by an evaporation at low pressure.<sup>2</sup> The work of Harkins and Broeker has been confirmed by Harkins and Hayes in an entirely independent separation of the isotopes of chlorine by the use of the same method as before,<sup>3</sup> a difference in density of 1.1 parts per thousand being obtained. In the work on chlorine very elaborate purifications were made with the materials obtained, before the density determinations were made. This makes the evidence for the separation conclusive.

Preliminary to more extensive work on the separation of isotopes, and as a guide to the choice of favorable substances for experimental work, the theory of the separation of isotopes by various types of diffusion or by non-equilibrium evaporation has been studied. Equations have been developed which show the rate of separation to be expected in such processes, for any given mixture of isotopes. A classification of methods which have been proposed for separating isotopes is also given. Molecular isotopes are discussed, and formulas are given for calculating the number and mol-fractions of the various molecular isotopes of a compound containing given isotopic elements. With the intention of comparing the efficiencies of the diffusion and evaporation methods, a partial separation of mercury into isotopes has been made, amounting to a difference in density of 133 parts per million. This is important in that it confirms the work of Brönsted and von Hevesy who, in their presumably preliminary note, give no special evidence that their mercury was entirely pure. Furthermore, the results agree completely with the theory which is developed in this paper.

<sup>1</sup> Harkins, *Phys. Rev.*, 15, 74 (1920); *Science*, N. S., 51, 289-291 (1920); *Nature*, 105, 230-1 (1920).

<sup>2</sup> Brönsted and von Hevesy, *Nature*, 106, 144 (1920).

<sup>3</sup> Harkins and Hayes, *THIS JOURNAL*, 43, 1803 (1921).

## Notation.

(Letters preceded by a (\*) in the following list are always used with one of the subscripts 1, 2,  $a$ — $b$ — $s$ — $n$ , each of which is used to refer to a particular molecular species;  $a$  and  $b$  refer to *any* molecular species,  $s$  and  $n$  to the last of a set or series. Letters preceded by a (+) may be used with the subscript  $0$  to denote initial values of the quantities to which they refer, for example,  $N_0$ ,  $(N_1)_0$ ,  $(x_a)_0$ .

- (\*) $N$  = rate of flow in mols per sec.
- (+) $N$  = total number of mols of material in *residue* at any time during a diffusion
- (\*+) $N$  = number of mols of an individual component in the *residue*
- (\*+) $x$  = mol-fraction
- (\*) $x$  = increase in mol-fraction of a component over its initial value, in the residue; (\*) $\Delta^c x$ , in the *total condensate*; (\*) $\Delta^{ic} x$ , in the *instantaneous condensate*
- $M$  = ordinary (average) molecular weight
- (\*) $M$  = molecular weight of a particular isotope  
 $\Delta M$ ,  $\Delta^c M$ ,  $\Delta^{ic} M$ , increase in molecular weight of residue, total condensate, and instantaneous condensate, respectively
- $k^1_a$  =  $c\sqrt{M_1/M_a}$ , where  $c$  is between 2 and 1; for example  $k^1_1 = c\sqrt{M_1/M_1}$
- $k^1_1$  =  $c\sqrt{M_1/M_1} = 1$
- $R$  = gas constant
- $T$  = absolute temperature
- (\*) $p$  = saturated vapor pressure (or, gaseous pressure in general)
- $r$  = radius of capillary tube;  $l$  = length of same
- (\*) $\lambda$  = mean free path of gas molecules
- (\*) $\bar{c}$  = mean velocity of gas molecules
- (\*) $n$  = number of mols or molecules, per cc.
- (\*)  $\frac{\delta n}{\delta z}$  = concentration gradient
- (\*) $d_{1s}$ ,  $d_{2s}$ , etc. = distance between centers of molecules 1 and  $s$ , or 2 and  $s$ , respectively, at impact; for example  $d_{12}$ ,  $d_{21}$ . Note that  $d_{11}$  or  $d_{12}$  become  $d_1$  or  $d_2$
- $A$ ,  $A'$ ,  $B$ ,  $B'$  = (see Equations 5, 5', 7 and 7')
- $C = N_0/N$  = "cut"
- $D$ ,  $D'$ ,  $E$ ,  $E'$  = (see Equations 6A, 6A', 7A, 7A')
- $S$  =  $\Sigma(x_a k^1_a) = x_1 + x_2 k^1_2 + \dots + x_n k^1_n$
- $n_0$  = number of atoms of an isotopic element in a compound; e. g., for  $\text{CCl}_4$ ,  $n_0 = 4$

## The Theory of Diffusion.

**The Flow of a Gas Through Small Openings. Molecular Diffusion.**—Graham<sup>4</sup> in his work on the passage of gases through porous membranes, distinguishes (1), *effusion* through small apertures, in which there is practically no friction, different gases developing a mass motion whose velocity is inversely proportional to the square root of the molecular weight; (2), *capillary transpiration*, in which the rate of mass motion is greatly reduced by friction, and obeys Poisseuille's law, with a slip term added at low pressures; and (3), *molecular diffusion*, in which mass motion is absent

<sup>4</sup> Graham, *Phil. Trans.*, 153, 385 (1863).

and the molecules pursue independent devious paths along the very fine pores, colliding repeatedly with the walls, but very seldom with one another. As with effusion, the rates of molecular diffusion of different gases are inversely as the square roots of their molecular weights. In the former case, however, the relation applies only to the gas as a whole, but in the latter, to each molecular species individually. For this reason molecular diffusion leads to a partial separation of mixed gases, while the other two processes do not. Knudsen<sup>5</sup> has deduced theoretically and confirmed experimentally the relation,  $N$  (mols./sec.) =  $\frac{4}{3}\sqrt{2\pi/MRT} (r^2/l) (p_1 - p_2)$  for a gas of molecular weight  $M$  flowing through a cylindrical pore of radius  $r$  and length  $l$ , from a partial pressure  $p_1$  to a partial pressure  $p_2$ . For pores of any shape,  $N$  is proportional to  $(p_1 - p_2)/\sqrt{MRT}$ . These relations begin to break down when the pore-diameter increases above 0.2 to 0.1 the mean free path in the gas at the maximum total pressure in the pore. Their failure is apparently not serious, however, until the pore diameter is about equal to the mean free path. If the pores are larger the phenomenon begins to pass into that of capillary transpiration.

To secure full efficiency in the separation of isotopes by molecular diffusion, all capillary transpiration must evidently be avoided. This can be done by the choice of membranes of sufficiently small pore diameter, or for a given pore size, by making the maximum pressure sufficiently low. If the efficiency is perfect, the rate of diffusion of any isotope ( $a$ ) in a mixture will be  $Kx_a/\sqrt{M_a}$ , where  $K$  is the same for all such isotopes present, for any set of conditions. The efficiency of the separation will be cut down by back diffusion if there is any back pressure of the isotopic mixture on the vacuum side.<sup>6</sup> Another important factor in efficiency is perfect mixing of the gas on the inner side of the membrane.

Molecular diffusion into a *vacuum* has been termed by Graham "single diffusion" or "atmolysis." When two gases (usually at equal total pressure) diffuse molecularly through a membrane from opposite sides, the phenomenon is called "double diffusion." This must be just as effective for the separation of isotopes as single diffusion, since the motions of the various molecular species are wholly independent. This method has also the advantage, provided a membrane containing fine enough pores can be secured, that it can be carried out at atmospheric pressure, the second gas being used in this case to sweep away the diffusate. If the pores are too large, relatively to the pressure, for double molecular diffusion, either capillary transpiration or ordinary gaseous diffusion, or a mixture of the two, will occur, depending on the magnitude of the pressure drop through the membrane.

**Gaseous Diffusion.**—When a gaseous mixture of isotopes and another

<sup>5</sup> Knudsen, *Ann. Phys.*, [4] 28, 75 (1908).

<sup>6</sup> See discussion on a later page, "Effect of Back Pressure on Efficiency."



gas interdiffuse through a porous membrane, a separation of isotopes should occur if there is a constant renewal of the two gases, as by flow along the membrane. This is the method used in the separation of the isotopes of hydrogen chloride by Harkins and his associates, who passed a stream of hydrogen chloride along the inside of clay pipes, and a stream of air along the outside. In their work the phenomenon was essentially gaseous diffusion, although there may have been some molecular diffusion.

Although gaseous diffusion as a method of separating isotopes considerably resembles molecular double diffusion, the theory is very much more complicated. The difference is due to the effects of collisions between molecules, which occur in the former case, but not in the latter. In the absence of mass motion, the rate of diffusion of one gas into another is given by  $N_1$  (mols/sq. cm./sec.)  $= (1/3) \lambda_1 \bar{c}_1 \delta n_1 / \delta z$ . For the case under consideration, the relative rate of diffusion of 2 isotopes should be given by

$$\frac{N_2}{N_1} = \frac{\lambda_2 \bar{c}_2 \delta n_2 / \delta z}{\lambda_1 \bar{c}_1 \delta n_1 / \delta z} = \sqrt{\frac{M_1}{M_2}} \cdot \frac{\lambda_2 \delta n_2 / \delta z}{\lambda_1 \delta n_1 / \delta z}.$$

The mean free path  $\lambda$ , of one molecular species in a mixed gas is dependent on the molecular weights, mol-fractions, and molecular diameters of all the various components. According to Jeans,<sup>7</sup> the value of  $\lambda_1$ , taking into account persistence of ve-

locities, is given by  $\lambda_1 = \frac{1}{\pi \Sigma [n_a d_{1a}^2 (1 - \theta_{1a}) \sqrt{1 + M_1/M_a}]}$  where  $\theta_{1a} =$

$(m_1 - \alpha_{1a} m_a) / (m_1 + m_a)$ ,  $\alpha_{1a}$  being a function of  $M_a / M_1$ . In the summation, the subscript  $a$  applies to each type of molecule present, 1, 2, —  $a$ , —  $s$ , in turn. Neglecting the effect of the persistence term  $(1 - \theta)$ , it is found by considering several limiting cases, assuming always that the molecular diameters of isotopes are equal, that  $\lambda_2 / \lambda_1$  has usually and on the whole a value equal to about  $\sqrt[4]{M_1 / M_2}$ , so that the ratio  $N_2 / N_1$  is increased to about  $(M_1 / M_2)^{3/4}$ . For a steady state,  $N_1$  and  $N_2$  have constant values, so that the concentration gradients must be uniform, except in compensation for the variation of  $\lambda_1$  and  $\lambda_2$  from point to point along the gradients. The concentrations of the isotopic substances and the corresponding gradients will of course decrease continuously along the length of the diffusion tube. This adds another complication to the theory of the operation as a whole. If the gradients are assumed uniform at a given point in the tube, and the concentration of both isotopes is zero at the lower ends of the gradients, we have  $N_2 / N_1 = (x_2 / x_1) (M_1 / M_2)^c$ , where  $c$  is about  $3/4$ . On account of the various assumptions, this last figure cannot be considered very certain, but at least it is probable that the general relation stated, which is analogous to the relations for the other processes considered, holds good.

<sup>7</sup> Jeans, "Dynamical Theory of Gases," The University Press, Cambridge, 1916, pp. 268, 330.

In the above treatment, mass motion has been assumed absent. Practically, this is an almost impossible condition, since the rate of gaseous diffusion does not exceed that of capillary transpiration unless the pressure drop is reduced to a fraction of a millimeter of mercury, even for openings as small as 0.01 mm. in diameter. Even with no pressure drop at all, there is normally some mass motion in gaseous diffusion, due to the unequal rates of diffusion of the two gases in opposite directions. This mass motion could of course be balanced by a suitable pressure drop (just sufficient to give rise to an equal and opposite capillary transpiration). In the diffusion of hydrogen chloride into air, the necessary mass motion is one of the former gas outwards; this could be prevented by a suitable slight excess of pressure on the air side.<sup>8</sup> An *exact* balance could, however, hardly be obtained in practise. The actual relative rate of diffusion, when mass motion is present, will be given by

$$\frac{N_2}{N_1} = \frac{N_2 - x_2(N_1 + N_2 + N_s + N_{\text{cap. trans.}})}{N_1 - x_1(N_1 + N_2 + N_s + N_{\text{cap. trans.}})} = \frac{N_2 - Ax_2}{N_1 - Ax_1},$$

where  $N_s = \frac{1}{2}\lambda_s \bar{c}_s \delta n_s / \delta z = -\frac{1}{2}\lambda_s \bar{c}_s \left( \frac{\delta n_1 + \delta n_2}{\delta z} \right)$ , the term  $N_1 + N_2 + N_s$  repre-

senting the mass motion necessary to overcome the inequality between  $N_1 + N_2$  and  $N_s$ ; and  $N_{\text{cap. trans.}}$  representing the added mass motion due to any drop in total pressure, and obeying Poyseuille's law. The values of  $x_1$  and  $x_2$  vary along the concentration gradient from their initial values to zero, hence  $N_1$  and  $N_2$ , and therefore  $\delta n_1 / \delta z$  and  $\delta n_2 / \delta z$  must vary, in order that  $N_1$  and  $N_2$  may be constant. If the mass motion, measured by the  $Ax$  term, is *positive*, its effect is clearly to *cut down* the rate of separation of the isotopes, although the detailed theory is complicated. (It may be noted that the gradual enrichment of the lighter isotope along the gradient reduces somewhat the effect of the  $Ax$  term.) If the mass motion is *negative*, the effect is apparently to *increase* the rate of separation of isotopes. A negative mass motion may however result in increased terminal pressure of the diffusing gas, which would again tend to decrease the rate of separation. A very rapid negative mass motion will of course practically prevent any diffusion.

A possible cause of loss of efficiency in gaseous diffusion is local convective action, due to unevenness in the texture of the membrane. In general, the theory of gaseous diffusion as applied to the separation of isotopes is evidently very complicated, but the relation  $N_2/N_1 = (x_2/x_1)(M_1/M_2)^c$  is probably approximately correct on the whole, the value of  $c$ , however, being uncertain and variable but probably greater than  $\frac{1}{2}$  in many cases.

<sup>8</sup> In the work of Harkins and his associates the pressure was kept slightly higher on the air side.

**Molecular Effusion and Non-equilibrium Evaporation.**—The rate of effusion through minute orifices,—of diameter not greater than one-tenth of the mean free path, according to Knudsen,<sup>9</sup> should from kinetic theory obey the law  $N = (p_1 - p_2) / \sqrt{2\pi MRT}$ , per square centimeter of opening. For larger openings, the phenomenon passes into that of mass effusion. As in the case of molecular diffusion, molecular effusion of two gases in opposite directions simultaneously can occur. The evaporation of a liquid in a vacuum, if no molecules return to the evaporating surface after they have once escaped, is equivalent to molecular effusion of the saturated vapor into a vacuum ( $p_2 = 0$ ), and obeys the same law (see below). The field of force at the surface acts like a membrane with very fine pores and negligible interspaces. Molecular diffusion passes into molecular effusion when the length of the pores approaches their diameter. Both processes, as well as the mixed process, should be equally effective in the separation of isotopes.

**Initial Diffusion Methods.**—In the expansion of a gas or in effusion or evaporation into a vacuum, it would be expected that the lighter molecules would get ahead, due to their higher average velocity, so that there would be an enrichment of these in the front rank molecules, which could be utilized if the latter could be separated from the molecules that follow. The separation would not be complete or even large, however, because of the *distribution* of velocities about the mean, for each molecular species. A somewhat analogous effect must occur in the front rank molecules at the beginning of a gaseous diffusion. Although a considerable enrichment might occur as the result of such a process, the material would be small in amount and difficult to collect.<sup>10</sup>

### Theory of Non-equilibrium Evaporation.

From kinetic theory, the number of mols of a vapor which strike one sq. cm. of the surface of a pure liquid in equilibrium with it, and so necessarily the number of mols of liquid which evaporate, per second, is  $N =$

$$\frac{p}{\sqrt{2\pi MRT}}.^{11}$$

For an ideal solution such as a mixture of isotopes, the re-

<sup>9</sup> Knudsen, *Ann. Phys.*, [4] 28, 999 (1909).

<sup>10</sup> Kohlweiler's report (*Z. physik. Chem.*, 95, 95-120 (1920)) of a considerable concentration of the lighter isotope of iodine is apparently an attempted application of this type of method. His theoretical treatment seems however to be unsound, and his experimental results are contrary to Aston's finding by positive-ray methods that iodine contains only one atomic species.

<sup>11</sup> For an excellent discussion of the derivation of this formula, first used by Hertz (*Ann. Phys.*, 17, 177 (1882)), and tested for mercury by Knudsen (*Ann. Phys.*, 47, 697 (1915)), see Langmuir, *Phys. Rev.*, [2] 2, 329 (1913). Knudsen found that the rate of evaporation fell far below that calculated unless the mercury surface was kept

lation  $N_a = \frac{px_a}{\sqrt{2\pi MRT}}$  should hold for each isotopic component ( $a$ ), if the vapor pressure has the same value ( $p$ ) for each such component when pure. That this is at least very closely true is shown by Aston's failure to obtain any separation of the isotopes of neon by 3000 fractionations, and by other evidence.<sup>12</sup> In an ordinary distillation, the rate of distillation is negligibly small compared with  $N$ , and there is practical equilibrium between liquid and vapor. Although lighter molecules evaporate faster from the liquid, they also return faster from the vapor, so that the two phases have practically the same isotopic composition. If, however, the pressure is made very low, and the condensing surface placed so close to the evaporating surface that practically all the evaporating molecules are condensed, it is clear that the condensate must be enriched in the lighter isotopes. This method of evaporation, as has already been seen, is really equivalent to molecular effusion.

The molecules leaving a liquid surface move forward with various velocities and in various directions. The farther a molecule has to travel before reaching a cold surface, the greater is its chance of collision with another molecule; and the greater the number of collisions it suffers, the more likely it is to acquire a backward component of velocity. If there are many collisions per molecule, the condition of a saturated vapor is approached, and the efficiency of the separation is reduced. The presence of air-molecules, which, being non-condensable, will be moving in all directions, will increase the number of unfavorable collisions. For maximum efficiency, (1) the apparatus must be thoroughly evacuated, (2) the rate of evaporation must be sufficiently low, and (3) the condensing surface must be as close as possible to the evaporating surface. Practically, at least in the case of mercury, as is shown by the present experimental work, the atoms can move through a distance equal to several times the mean free path for the saturated vapor, and can suffer a number of collisions, without much loss of efficiency.

In order that the theoretical efficiency shall be attained, the evaporating liquid must be kept at a uniform composition throughout, by diffusion, convection, or by artificial mixing. Otherwise the accumulation of heavy molecules in the surface will cause a corresponding increase in their proportion in the condensate. Approximate calculations indicate, however, that liquid diffusion alone is capable of preventing more than a slight loss of efficiency, even for fairly considerable rates of evaporation. This is very clean, as by constant renewal. The exact formula for the rate of evaporation is  $N = (1-r) p \sqrt{2\pi MRT}$ , but  $r = 1$ , practically, for a liquid and its saturated vapor.

<sup>12</sup> In view of the thermodynamic relation between vapor pressure and solubility, the failure of Richards and Hall (*THIS JOURNAL*, 39, 531 (1917)), to secure any change of atomic weight by 1000 recrystallizations of lead nitrate from radioactive material, is additional evidence for the very close equality of the vapor pressures of isotopes.

in harmony with the experimental results. Because of the impossibility of rapid mixing, the separation of isotopes by evaporation from a solid surface is evidently impracticable. The range of application of the method may however be extended by the use of solvents.

**Comparison of Methods.**—The choice of elements suitable for separation by evaporation is limited to those forming suitable compounds or solutions or themselves existing as liquids having a small vapor pressure at a convenient temperature. To be suitable for a diffusion method, a substance must exist as a gas or have a considerable vapor pressure preferably at room temperature. The diffusion method probably has wider applicability than the evaporation method.

### Development of Equations Showing Rate of Change of Composition and Atomic Weight in Diffusion Processes.

**Change in Composition of Residue for the Case of Two Isotopes.**—For a mixture of two isotopes having molecular weights  $M_1$  and  $M_2$ , and mol-fractions  $x_1$  and  $x_2$ , the relative rate of molecular diffusion, molecular effusion, or evaporation, is given by

$$-dN_2/-dN_1 = (x_2/\sqrt{M_2}) (\sqrt{M_1}/x_1) = (x_2/x_1) \sqrt{M_1/M_2} = k_2^1 (x_2/x_1). \quad (1)$$

$N_1$  and  $N_2$  denote the respective numbers of mols of the two isotopes in the *residue* at any time.  $N$  will be used to denote  $N_1 + N_2$ , and  $N_0$  to denote the number of mols initially present. For gaseous diffusion, the relation is the same, except that  $k_2^1$  means  $c\sqrt{M_1/M_2}$ , where  $c$  is some number between 1 and 2. Rearranging Equation 1 and noting that  $N_1 = N \cdot x_1$  and  $N_2 = N \cdot x_2$

$$dN_2/x_2 = k_2^1 dN_1/x_1, \text{ or } \frac{Nd x_2 + x_2 dN}{x_2} = k_2^1 \left( \frac{Nd x_1 + x_1 dN}{x_1} \right).$$

$$\text{Then, } (1-k) dN/N = k \left( \frac{dx_1}{x_1} \right) - \frac{dx_2}{x_2}. \quad (2)$$

Integrating,

$$(1-k) \ln N/N_0 = k \ln (x_1/(x_1)_0) - \ln (x_2/(x_2)_0).$$

Or, denoting  $N_0/N$ , the "cut," by  $C$ ,

$$(1-k) \log C = k (\log(x_1)_0 - \log x_1) - \log (x_2)_0 + \log x_2. \quad (3)$$

This equation can be used to calculate the cut necessary to obtain any desired change in the composition of the residue, the initial composition being known. The change in atomic weight of the residue for a given change in composition may be obtained from the relation,  $\Delta M = (M_2 - M_1) \Delta x_2$ .<sup>13</sup>

<sup>13</sup> In general, for a mixture of ( $n$ ) isotopes, if the atomic or molecular volumes are equal, as the work of Soddy (*Nature*, 94, 615 (1915)), and of Richards and Wadsworth (*This Journal*, 38, 221 (1916)) shows to be true in the case of the atomic volume of solid lead,  $\Delta M = (M_2 - M_1) \Delta x_2 + (M_3 - M_1) \Delta x_3 + \dots + (M_n - M_1) \Delta x_n = \Sigma (M_i - M_1) \Delta x_i$ . This relation applies to mixtures of isotopic atoms or of isotopic molecules, i. e., molecules differing only in containing atoms which are isotopes of each other, e. g.,  $\text{HCl}_{35}$  and  $\text{HCl}_{37}$ ;  $\text{CH}_3(\text{Cl}_{35})_2$ ,  $\text{CH}_3\text{Cl}_{35}\text{Cl}_{37}$ , and  $\text{CH}_3(\text{Cl}_{37})_2$ ;  $\text{Mg}_{24}\text{O}$ ,  $\text{Mg}_{25}\text{O}$ , and  $\text{Mg}_{26}\text{O}$ .

For the diffusate, the change,  $\Delta'M$ , is exactly  $-\Delta M/(C-1)$  (see Equation 14 p. 49). In connection with his work on the separation of the rare gases, Rayleigh<sup>14</sup> developed a less direct but simpler equation, which is rather more convenient for calculation than Equation 3. He uses the term enrichment ratio, symbolized by  $r$ , for  $\frac{x_2/(x_2)_0}{x_1/(x_1)_0}$ . Using

the symbols of the present paper, Rayleigh's relation can be reduced<sup>15</sup> to

$$C = [x_1/(x_1)_0] \cdot r^{1/(1-k)} \quad (4)$$

This is readily obtained from (3). If  $r$  is near unity, Equation 4 becomes, very nearly,  $C = r^{1/(1-k)}$ . In making calculations of  $C$  in terms of  $\Delta M$  or  $\Delta x$ , the easiest method is to calculate  $1/(1-k)$  (compare the table p. 55) once for all for the compound under consideration, then to calculate the value of  $r$  corresponding to the assumed value of  $\Delta M$  or  $\Delta x$ , and finally to apply Equation 4.  $\Delta'M$ , the decrease of atomic weight for the diffusate, equals  $-\frac{\Delta M}{C-1}$ .

**Simple Equations for Change of Composition of Residue for Small Cuts.**—The use of the exact relations (3) and (4) involves much calculation. For small cuts, or approximate calculations with larger cuts, a very simple relation, which shows clearly the factors governing the rate of separation, can be derived from Equation 2. Noting that  $dx_1 = -dx_2$ , Equation 2 becomes  $(1-k) dN/N = (-k/x_1)dx_2 - dx_2/x_2$ . Noting that  $-dN/N = \frac{-d(N/N_0)}{N/N_0} = d \ln C$ , this reduces to

$$dx_2 = -dx_1 = \frac{(1-k)x_1x_2}{x_1 + kx_2} \cdot d \ln C = A d \ln C. \quad (5)$$

This quantity  $A$  is really the slope, at the point  $(x_2, \ln C)$ , of the curve obtained by plotting  $x_2$  (or  $-x_1$ ) against  $\ln C$ , starting with  $C=1$  for  $x_1=(x_1)_0$  and  $x_2=(x_2)_0$ . As the composition changes only very slowly with the cut,  $A$  is nearly a constant, so that

$$\Delta x_2 = \frac{(1-k)x_1x_2}{x_1 + kx_2} \ln C, \text{ nearly.} \quad (6)$$

By taking average values of  $x_1$  and  $x_2$  this equation will hold rather closely even for a large cut. For the change in atomic weight of the residue,

$$\Delta M = (M_2 - M_1) \Delta x_2 = \frac{(1-k)x_1x_2(M_2 - M_1)}{x_1 + kx_2} \ln C = B \ln C. \quad (7)$$

<sup>14</sup> Rayleigh, *Phil. Mag.*, [5] 42, 493 (1896).

<sup>15</sup> Harkins and Hayes (Ref. 3) use a similar form of Rayleigh's equation. The (negative of the) quantity  $1/(1-k)$  of this paper, which is the exponent of  $r$  in Equation 4, is termed the "diffusion coefficient" in their paper, and a rule is given for calculating this quantity. This rule and the relations of the quantities mentioned are discussed in a note on a subsequent page, under the head of "Useful Approximate Forms of Simple Equations."

Note that  $C$  is strictly a ratio of mols, or of volumes. Unless  $C$  is extremely large, however, it may without much error be considered a ratio of masses. From Equations 6 and 7 it is seen that the increase in the mol-fraction of heavy isotope and in the atomic weight of the residue proceed arithmetically as the quantity of the latter diminishes exponentially.

**Relation of Rate of Separation to Composition of an Isotopic Mixture.**—The rate at which  $A$  and  $B$  change with the composition or atomic weight of the residue during a diffusion or evaporation can be obtained to a close approximation as follows. Since  $x_1 + kx_2$  is always nearly unity, we can write

$$A = \left( \frac{1-k}{x_1+kx_2} \right), \quad x_1x_2 = Fx_1x_2, \text{ and } B = \frac{1-k}{x_1+kx_2} \quad (M_2 - M_1)x_1x_2 = Gx_1x_2, \quad F \text{ and } G$$

being regarded as essentially constant. Then

$$\frac{dA}{dx_2} \left( -\frac{dB}{dM} \right) = F \frac{d(x_1x_2)}{dx_2} = F \frac{d(x_2-x_2^2)}{dx_2} = F(1-2x_2) = F(x_1-x_2) = \frac{A(x_1-x_2)}{x_1x_2} \quad (8)$$

If values of  $A$  or  $B$  are plotted as ordinates against values of  $x_2$  (or  $-x_1$ ) as abscissas, a portion of a parabola is obtained, corresponding to the equation  $A = Fx_1x_2 = F(x_2-x_2^2)$ , or  $B = G(x_2-x_2^2)$ . This begins at the point ( $x_2=0$ ,  $A$  or  $B=0$ ), rises to a maximum at ( $x_2=0.50$ ,  $A=0.25F$  or  $B=0.25G$ ), and falls again to ( $x_2=1$ ,  $A$  or  $B=0$ ). Thus the most favorable mixture for the separation of two given isotopes is that for which  $x_1 = x_2 = 0.50$ . Between  $x_2=0.25$  and  $x_2=0.75$  the value of  $B$  is still nearly as favorable, but if  $x_2$  falls below 0.05 to 0.10, or rises above 0.90 to 0.95, the rate of separation is much reduced. If  $x_2$  (or  $M$ ) is plotted against  $\ln C$  for the residue, the slope  $A$  (or  $B$ ) of this curve thus approaches zero, and the curve itself approaches asymptotically the line  $x_2=1$  (or  $M=M_2$ ), as  $\ln C$  continues to increase; the curve is terminated abruptly in the other direction at  $C=1$ .

The slope  $dA/dx_2$  of the  $A$  parabola is given by Equation 8. Since  $B = (M_2 - M_1) A$ , and  $\Delta M = (M_2 - M_1) \Delta x_2$ , it is evident that  $dB/dM$  is equal to  $dA/dx_2$ . From Equation 8, then,  $dB/dM$  is zero when  $x_2=0.50$ , has a maximum positive value when  $x_2=0$ , and a maximum negative value when  $x_2=1$ . Thus  $B$  (and  $A$ ) increase for the residue (and decrease for the diffusate), during a separation, if  $x_2$  is less than  $x_1$ ; and *vice versa*.

**Modifications of Simple Equations for Large Cuts.**—The quantity  $\frac{dB/B}{dM}$  is useful as a measure of the error in  $B$  when  $\Delta M$  is large.

$$\frac{dB/B}{dM} = \frac{F(x_1-x_2)}{B} = \frac{x_1-x_2}{x_1x_2(M_2-M_1)}.$$

Call this last quantity  $2H$ . For a moderately large change  $\Delta M$  of atomic weight we have, approximately,

$$\Delta M = \left[ B + \frac{1}{2} \left( \frac{dB}{dM} \right) \Delta M \right] \ln C = B \left[ 1 + \frac{1}{2} \left( \frac{dB/B}{dM} \right) \Delta M \right] \ln C = B(1 + H \Delta M) \ln C. (9)^{10}$$

For the case that  $M_2 - M_1 = 2$ , if  $x_2 = 0.01$ , the value of  $H$  is 24.8; if  $x_2 = 0.10$ ,  $H = 2.22$ ; if  $x_2 = 0.25$ ,  $H = 0.67$ ; if  $x_2 = 0.50$ ,  $H = 0$ ; if  $x_2 = 0.75$ ,  $H = -0.67$ ; etc. The correction term  $H \Delta M$  is evidently not large unless  $\Delta M$  is considerable, or  $x_2$  is near zero or unity. For ordinary hydrogen chloride,  $x_2 = 0.23$ ,  $B = 0.00950$ , and  $H = +0.76$ . Without using the correction term, we have, for  $\Delta M = 0.05$ ,  $\Delta M = 0.05 = 0.00950 \ln C$ . By putting in the correction term,  $\Delta M = 0.05 = 0.00950 (1.038) \ln C$ . The value of  $C$  calculated from the former expression (Equation 7) is 192.7; that from the latter (Equation 9) is 158.9. The *correct* value of  $C$ , calculated by means of Equation 4, is 159.8. For  $\Delta M = 0.10$ , the respective values of  $C$  obtained by the three methods are 37,140; 17,630; and 18,530. The discrepancies between the results of Equation 4 and Equation 7 are not large, especially from the point of view of the change of atomic weight secured by a given cut, and are in fact much less than would normally result between theory and practise due to unavoidable inefficiency of operation. Equation 9 evidently gives a very close approximation to the results of the exact Equation 4, and is much simpler than the latter, once the values of  $B$  and  $H$  have been calculated for the compound under consideration. Values of  $B$  are given in Table I p. 55. Equation 10 which likewise gives a very close approximation, is useful for calculating  $\Delta M$  if  $C$  is given.

**Useful Approximate Forms of Simple Equations; Relation of Rate of Separation to Molecular Weights of Isotopes.**—The term  $(1-k)$  in Equations 6 and 7 can be calculated very quickly and accurately by means of the approximate empirical relation  $(1-k) = (4/c) (M_2 - M_1) / (3M_2 + M_1)$ . This is correct to within about 0.1% for the lightest elements, and is *still more exact* for the heavier elements. For example, the exact value of  $1-k$ , for  $c=2$ , and  $M_1=6$  and  $M_2=7$ , is 0.074180, while that calculated from the above relation is 0.074074, or 0.14% too low. For  $M_1=36$ ,  $M_2=38$ , the exact value of  $1-k$  is 0.026672, and the approximate value 0.026667; the latter is only 0.018% low. Using the relation just given, Equation 6 becomes

$$\Delta x_2 = \frac{(M_2 - M_1)x_1x_2}{(c/4)(3M_2 + M_1)(1 - (1-k)x_2)} \ln C = A \ln C \text{ (practically)}. \quad (6B)$$

and Equation 7 becomes

$$\Delta M = \frac{(M_2 - M_1)^2x_1x_2}{(c/4)(3M_2 + M_1)(1 - (1-k)x_2)} \ln C = B \ln C \text{ (practically)}. \quad (7B)$$

$A$  and  $B$  can be calculated with sufficient accuracy in accordance with these equations, the term  $(1 - (1-k)x_2)$  being readily calculated by the help of

<sup>10</sup> Since  $\Delta M \approx B \ln C$ , nearly, this can also be written,

$$\Delta M = B(1 + BH \ln C) \ln C. \quad (10)$$



the relation given. This term can be neglected entirely for neon and heavier elements, when an accuracy of 1% is sufficient, giving simplified forms of Equations 6B and 7B which may be called Equations 6BB and 7BB. These can be still further simplified to<sup>17</sup> the still less exact forms,

$$\Delta x_2 = [(M_2 - M_1)x_1x_2/cM_2] \ln C = D \ln C \quad (6A)$$

and

$$\Delta M = [(M_2 - M_1)^2x_1x_2/cM_2] \ln C = E \ln C \quad (7A)$$

This form of Equation 7 brings out the dependence of the "separation coefficient"  $B$  on the *total molecular weight* and on the *interval between the molecular weights* of the two isotopes. For calculations of the separation coefficient, Equation 7B is practically as exact as Equation 7; and Equation 7BB gives results which are very little in error, except for the lightest elements. The very simple approximation given by Equation 7A gives results at worst 3% low, for elements above neon, but in general Equation 7B or 7BB should be used.

**Change of Composition for Diffusate.**—While the residue is being enriched in the heavier isotopes, the diffusate or condensate is being enriched in the lighter isotopes. For the "instantaneous" diffusate or condensate coming from material of a given composition ( $x_1, x_2$ ) we can write

<sup>17</sup>  $(1-k) = 1 - \sqrt{M_1/M_2} = 1 - \sqrt{1 - (M_2 - M_1)/M_2} = 1 - \sqrt{1 - c(M_2 - M_1)/cM_2} = 1 - \sqrt{[1 - (M_2 - M_1)/cM_2]^c}$  (nearly)  $= 1 - [1 - (M_2 - M_1)/cM_2]$ , (nearly)  $= (M_2 - M_1)/cM_2$ , (nearly). The usual case is  $c=2$ , but the relation holds for any value of  $c$  (it is of course exact for  $c=1$ ), provided  $M_2 - M_1$  is small compared with  $M_2$ . The empirical relation  $(1-k) = (4/c) (M_2 - M_1)/(3M_2 + M_1)$  holds very closely even when  $M_2 - M_1$  approaches  $M_2$  in magnitude. This relation reduces to  $2(M_2 - M_1)/(3M_2 + M_1)$ , for  $c=2$ . This can be used for calculating  $B$  of Equation 7.

The quantity  $(1-k)$  is closely related to the "diffusion exponents"  $(k)$  and  $(k')$  of Harkins and Hayes.<sup>8</sup>  $(k)$  is equal to  $-1/(1-k)$ , and  $(k')$  to  $-1/(1-(1/k)) = +k/(1-k)$ . The "diffusion exponent" is the same (except for the sign) as the exponent

of  $r$  in Equation 4 of this paper. The rule of Harkins and Hayes that  $\frac{(k) + (k')}{2} = (M_1 + M_2)/(M_1 - M_2)$ ,  $(k)$  and  $(k')$  being respectively 0.50 unit greater, or less, than  $(M_1 + M_2)/(M_1 - M_2)$ , agrees with the above empirical relation for  $1-k$ . [The relation  $(k) - (k') = 1$  is an exact and necessary one, for  $(k) = \sqrt{M_1}/(\sqrt{M_1} - \sqrt{M_2})$ , and  $(k') = \sqrt{M_2}/(\sqrt{M_1} - \sqrt{M_2})$ .] The approximations  $(1-k) = (M_2 - M_1)/cM_2$  [1], and the analogous  $(1-1/k) = (M_1 - M_2)/cM_1$  [2], are less exact than the approximations  $(1-k) = (4/c) (M_2 - M_1)/(3M_2 + M_1)$  [3], and  $(1-1/k) = (4/c) (M_1 - M_2)/(3M_1 + M_2)$  [4].

For, using [1] and [2], while  $\frac{(k) + (k')}{2} = (-1/2)[(1/1-k) + 1/(1-(1/k))]$ ,  $= \frac{M_1 + M_2}{M_1 - M_2}$ ,

comes out as it should, the result  $(k) - (k') = 2$  is obviously wrong. Using Equations [3] and [4] for  $(1-k)$  and  $(1-(1/k))$ ,  $(k) + (k') = (M_1 + M_2)/(M_1 - M_2)$ , and  $(k) - (k') = 1$ , as it should. The relation of Equation 3, and the corresponding relations,  $(k) = (3M_2 + M_1)c/4(M_1 - M_2)$ , and  $(k') = (3M_1 + M_2)c/4(M_1 - M_2)$ , prove to be so nearly exact that they can be used for calculations by the exact Equation 4.

$$(x_1)^{ic} = \frac{dN_1}{dN_1 + dN_2} = \frac{x_1 / {}^e\sqrt{M_1}}{x_1 / {}^e\sqrt{M_1} + x_2 / {}^e\sqrt{M_2}}.$$

From this can be obtained<sup>18</sup> the *exact* equations

$$(\Delta^{ic}x_1) = \frac{(1-k)x_1x_2}{x_1 + kx_2} = +A \quad (11)$$

and

$$\Delta^{ic}M = -(\Delta^{ic}x_1) (M_2 - M_1) = \frac{(1-k)x_1x_2(M_2 - M_1)}{x_1 + kx_2} = -B. \quad (12)$$

The composition of the instantaneous diffusate or condensate always keeps pace with that of the residue,  $x_1^{ic}$  being just A units ahead of  $x_1$ , and  $M^{ic}$  just B units behind  $M$  (see Fig. 1). The composition of the *total* diffusate is an average of a series of continuously-changing instantaneous diffusates. It obviously approaches that of the original material as the *quantity* of residue approaches the vanishing point. For a mixture of two or any number of isotopes the mol-fraction  $x_a$  of any component (a) in the total diffusate is necessarily

$$x_a^c = \frac{(N_a)_o - N_a}{N_o - N} = \frac{(x_a)_o N_o - x_a N}{N_o - N} = \frac{(x_a)_o C - x_a}{C - 1};$$

and

$$x_a^c - (x_a)_o = \Delta^c x_a = \frac{(x_a)_o C - x_a}{C - 1} - (x_a)_o = \frac{(x_a)_o - x_a}{C - 1} = \frac{-\Delta x_a}{C - 1} \quad (13)$$

where  $\Delta^c$ ,  $x_a^c$ , etc., refer to the diffusate,  $x_a$ ,  $\Delta$ , etc., to the residue. Correspondingly,

$$\Delta^c M = \Sigma(M_a - M_1) (\Delta^c x_a) = \frac{\Sigma(M_a - M_1) (-\Delta x_a)}{C - 1} = \frac{-\Delta M}{C - 1}. \quad (14)$$

Equations 13 and 14 must hold independently of the nature or efficiency of the diffusion process, and depend only on the assumption that isotopes have equal atomic or molecular volume. By means of these relations, for a 100% efficient process, we have at once,

$$\Delta^c x_a = -A \frac{\ln C}{C - 1} \quad (15)$$

and

$$\Delta^c M = -B \frac{\ln C}{C - 1}, \quad (16)$$

u

$$\frac{x_1 / {}^e\sqrt{M_1}}{x_1 / {}^e\sqrt{M_1} + x_2 / {}^e\sqrt{M_2}} = \frac{x_1^c \sqrt{M_2}}{x_1^c \sqrt{M_2} + x_2^c \sqrt{M_1}} = \frac{x_1}{x_1 + kx_2}$$

Then

$$x_1^{ic} - x_1 = \Delta^{ic}x_1 = \frac{x_1}{x_1 + kx_2} - x_1 = \frac{x_1 - x_1^2 - kx_1x_2}{x_1 + kx_2} = \frac{x_1 - x_1^2 - kx_1(1 - x_1)}{x_1 + kx_2} = \frac{(1-k)x_1x_2}{x_1 + kx_2}.$$

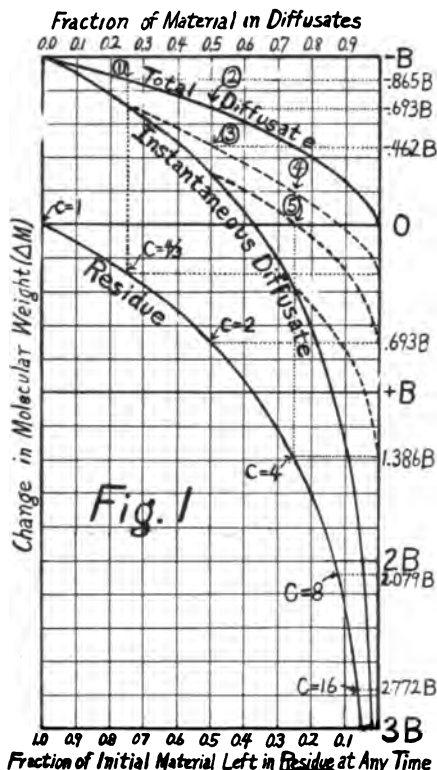


Fig. 1. Generalized plot showing atomic or molecular weight of fractions obtained during a 100% efficient diffusion or irreversible evaporation of a mixture of isotopes.

The curves are based on Equations 7, 12, and 16, of the text. The ordinates are expressed in terms of the "separation coefficient"  $B$  as a unit; this has a different numerical value (usually about 0.003 to 0.02) for each element (see Table I, and text). The value of  $B$  changes slightly with  $\Delta M$ . The symbol  $C$  stands for the "cut" or ratio of quantity of material in the residue at any time to the initial quantity; for any abscissa on the lower scale, the "cut" is merely the reciprocal quantity. The "instantaneous diffusate" curve gives at any point the composition of the material which is at any instant diffusing or evaporating from residual material corresponding to the same abscissa. Note that this curve has exactly the same form as the residue curve, and differs only in an upward displacement of the ordinates by  $B$  units. Each point on the "total diffusate" curve gives the average composition of the material which has diffused or evaporated from the beginning up to that point. The various dotted curves give the composition of fractions of the total diffusate beginning at various points after the beginning of the operation. The meaning of the total diffusate curves can be made clearer by a few examples. Thus, Point 1 gives the composition of the diffused or condensed fraction for the interval 0-25%; Point 2, for the interval 0-50%; 3, for 25-50%; 4, for 25-75%; 5, for 50-75%. Taken in connection with the residue curve, the total diffusate curves show how the original material can be divided efficiently into isotopic fractions. For example, the curves show that the diffusate might be collected in fractions as follows: 0-25%,  $\Delta M = -0.865B$ ; 25-50%,  $\Delta M = -0.462B$ ; 50-75%,  $\Delta M = 0$ . If the operation were stopped here, the residue would have the atomic or molecular weight  $M + 1.386B$ , if  $M$  is the original atomic or molecular weight.

and corresponding approximate relations with  $D$  and  $E$ . By putting  $C=1$  and noting that the limit of  $\ln C/(C-1)$  is unity, as  $C$  approaches unity, Equations 13 and 14 reduce to 11 and 12. For the result of  $n$  successive identical operations on the light fraction, equations analogous to 9 and 10 can be written, *viz.*,

$$\Delta^c M = -nB(1 + H\Delta^c M) \ln C/(C-1), \quad (17)$$

and

$$\Delta^c M = -nB[1 - BH \ln C/(C-1)] \ln C/(C-1), \quad (18)$$

where  $C$  is the cut in *each operation*.

**Systematic Fractionation.**—Large *decreases* of atomic weight can evidently be secured only by repeated operations, a nearly equal decrease being secured in each similar operation. With the residue on the other hand, large *increases* can be secured in a single operation by starting with sufficient material and making a large cut. A good practical compromise for systematic fractionation is a cut of 2. Here —  $\Delta^c M = \Delta M = \ln 2 = 0.693 B$ . The use of such a method has been discussed by Lord Rayleigh<sup>14</sup> who developed approximate formulas giving the size and quality of the various fractions. The collection of the whole diffusate together, especially for a cut as large as 2 or greater, involves considerable avoidable loss of efficiency. If it is collected in successive fractions as suggested by the plot (Fig. 1), successive cuts can be made on the *residue* in one operation. The total diffusate coming through between  $C=2$ , and  $C=4$  has practically the composition of the original material, and in quantity is 25% of the latter. In systematic fractionation, the actual changes in atomic weight will be less than the calculated if any of the causes of inefficiency previously discussed operate. The values of  $\Delta x$  and  $\Delta M$  given by Equations 6, 7, 11, 12, 15 and 16, etc., must be multiplied by an empirical efficiency factor which depends on the experimental conditions. Equations 3 and 4 are of course subject to a similar limitation. Equations 13 and 14 always hold (p. 49). The variation of  $\Delta x$  and  $\Delta M$  with large cuts has already been discussed under "Modifications of Simple Equations for Large Cuts." In general, efficiency and speed will be opposed. On this account, it may not be desirable to aim at the highest efficiency at the beginning of operations, when dealing with large quantities of material, but high efficiency becomes more and more worth while as the cut increases.

**Effect of Back Pressure on Efficiency.**—In molecular diffusion and molecular effusion, the fractional loss of efficiency due to back pressure is equal to the ratio of the back pressure to the initial pressure. This is shown by the following considerations. The *actual* increase,  $\overline{\Delta x}$ , in the mol-fraction of any isotope in the diffusate, may be considered as the net result of two processes, forward and backward diffusion, which can be treated as independent (see earlier discussion). Letting  $\Delta x$  denote the

increase for a 100% efficient process, and  $N_1$  and  $N_2$  the quantities of material which diffuse forward and backward, respectively, we can write,

$$\overline{\Delta x} = \frac{N_1 \overline{\Delta x} - N_2 (\overline{\Delta x} + \Delta x)}{N_1 - N_2}.$$

Simplifying,

$$\overline{\Delta x} = \left( \frac{N_1 - N_2}{N_1} \right) \Delta x = \left( \frac{p_1 - p_2}{p_1} \right) \Delta x.$$

The efficiency of the process is  $\overline{\Delta x} / \Delta x$ , and is thus equal to  $\frac{p_1 - p_2}{p_1}$ ; and the loss of efficiency is  $p_2 / p_1$ . Analogous considerations apply to non-equilibrium evaporation, if  $p_1$  and  $p_2$  now stand for rate of evaporation and rate of return of molecules, respectively. With gaseous diffusion the case is more complicated, but analogous effects are to be expected.

**General Relations for Any Number of Isotopes.**—For the general case of a mixture of  $n$  isotopes, exact and approximate slope equations analogous to (5), (6), and (7) can be obtained in the following way.  $N$  separate equations of the form of Equation 1 can be written, *viz.*,

$$dN_a / x_a = k^1_a dN_1 / x_1 \quad (1')$$

and correspondingly,  $n$  equations of the form of Equation 2, *viz.*,

$$(1 - k^1_a) dN / N = k^1_a dx_1 / x_1 - dx_a / x_a. \quad (2')$$

The equation for which  $a=1$  is included for the sake of generality in the subsequent development. It is convenient to write all the equations in terms of the lightest component, (1), although any other component could have been chosen. From the  $a^{\text{th}}$  equation of the form of (2), one can get  $dx_a = k^1_a (x_a / x_1) dx_1 - x_a (1 - k^1_a) dN / N$ . Now it is evident that  $\sum dx = 0$ . Then

$$\sum dx_a = \sum [k^1_a (x_a / x_1) dx_1 - (1 - k^1_a) x_a dN / N] = 0.$$

Or,

$$(dN / N) \sum (x_a - x_a k^1_a) = (dx_1 / x_1) \sum x_a k^1_a.$$

Or,

$$(dN / N) (1 - \sum x_a k^1_a) = (dx_1 / x_1) \sum x_a k^1_a.$$

Denoting  $\sum x_a k^1_a$  by  $S$ , this becomes  $\frac{1-S}{S} \cdot \frac{dN}{N} = dx_1 / x_1$ . By substituting the value  $dx_1 / x_1 = (1 / k^1_a) [(1 - k^1_a) dN / N + dx_a / x_a]$ , obtained from equation (2'), and simplifying, the general expression for any isotope ( $a$ ),

$$dx_a = \frac{x_a (k^1_a - S)}{S} \cdot dN / N = \frac{x_a (S - k^1_a)}{S} \cdot d \ln C = A'_a d \ln C, \quad (5')$$

is obtained. This is the general form of the slope Equation 5, and can be treated like the latter. Thus

$$\Delta x_a = \frac{x_a (S - k^1_a)}{S} \ln C, \text{ nearly.} \quad (6')$$

Since  $\Delta M = \Sigma[(M_a - M_1) \Delta x_a]$ ,

$$\Delta M = \frac{\Sigma[(M_a - M_1)x_a(S - k^1_a)]}{S}. \quad \ln C = B' \ln C, \text{ nearly.} \quad (7')$$

This summation has  $n$  terms. It can be shown<sup>10</sup> that the following relation also holds approximately

$$\Delta M = \frac{\Sigma x_a x_b (M_a - M_b)^2}{cM}. \quad \ln C = E' \ln C \quad (7A')$$

where  $a$  and  $b$  take independently every value from 1 to  $n$ , like terms, however, being taken only once. This summation has  $\frac{n(n-1)}{2}$  different terms. The calculation of  $E'$  is simpler than that of  $B'$  if  $n$  is not too large; and  $E'$  usually approximates  $B'$  very closely (see table of separation coefficients). The equations for the condensate are very easily generalized. Equations 11 and 12 become

$$\Delta^{ic} x_a = -A'. \quad (11')$$

and

$$\Delta^{ic} M = -B'. \quad (12')$$

Equation 13 holds as it stands for any isotope  $a$ , and Equation 14 for the case of  $n$  isotopes; Equations 15 and 16 become

$$\Delta^c x_a = -A' \cdot \frac{\ln C}{C-1} \quad (15')$$

and

$$\Delta^c M = -B' \cdot \frac{\ln C}{C-1}. \quad (16')$$

<sup>10</sup> Since  $1 = \Sigma x$ , we can write  $S - k^1_a = (x_1 k^1_1 + x_2 k^1_2 + \dots + x_n k^1_n) - (x_1 + x_2 + \dots + x_n) k^1_a = x_1(k^1_1 - k^1_a) + x_2(k^1_2 - k^1_a) + \dots + x_n(k^1_n - k^1_a)$ . In general  $k^1_b - k^1_a = (1 - k^1_a) - (1 - k^1_b) = (M_a - M_1)/cM_a - (M_b - M_1)/cM_b$ , nearly, (see note on earlier page),  $= (M_1/c) (M_a - M_b)/M_a M_b$ . Applying this relation to the expression for  $S - k^1_a$ , the latter becomes  $(M_1/c) (1/M_a) \Sigma [x_b (M_a - M_b)/M_b]$ , where the subscript  $b$ , like  $a$ , stands for all numbers from 1 to  $n$ , to be chose, however, independently of the series of values for  $a$ . By application of this relation, Equation 5 can be written approximately,  $dx_a = (x_a/c) \Sigma [x_b (M_a - M_b)/M_b] \cdot d \ln C$  (5A'), since  $S$  is very nearly unity.

The summation in Equation 7' can be simplified as follows.  $\Sigma (M_a - M_1) x_a (S - k^1_a) = \Sigma M_a x_a - \Sigma M_a x_a k^1_a = \Sigma M_a x_a - \Sigma M_a x_a k^1_a - \Sigma M_1 x_a k^1_a = \Sigma M_a x_a - \Sigma M_a x_a k^1_a - \Sigma M_1 x_a k^1_a = \Sigma (M_a - M_1) x_a (S - k^1_a)$ . Equation 7' then becomes  $\Delta M = \frac{\ln C}{S} \Sigma (M_a x_a) (S - k^1_a)$ . Applying the relation already obtained for  $S - K^1_a$ ,

$$\Delta M = [(M_1 \ln C)/cS] \cdot \Sigma [(M_a x_a (1/M_a)] \Sigma [x_b (M_a - M_b)/M_b].$$

This readily reduces to  $\Delta M = (M_1/c) \frac{(\ln C)}{S} \cdot \Sigma (x_a x_b (M_a - M_b)^2 / M_a M_b)$ .

This gives the closely approximate relation

$$\Delta M = \frac{\ln C}{cM} \cdot \Sigma [x_a x_b (M_a - M_b)^2] \quad (7A'')$$

### Factors Determining Rate of Separation and Table of Separation Coefficients for Natural Isotopic Mixtures.

Equations 6' and 7' show that the close proportionality between  $\Delta M$  and  $\ln C$  holds for a mixture of any number of isotopes as well as for two isotopes. The approximate constant  $B$  for any element or compound can thus be determined experimentally by means of a 100% efficient diffusion or evaporation, without knowing the isotopic composition. In the following table are given values of the exact coefficients  $B$ , or  $B'$ , and of the approximate coefficients  $E$ , or  $E'$ , calculated for  $c=2$ , for various naturally occurring isotopic mixtures. It should be noted that the approximation of  $E'$  to  $B'$  is much closer than that of  $E$  to  $B$ , so that while  $E'$  satisfactorily replaces the more complicated  $B'$ ,  $B$  should be calculated, by one of the more exact equations 7B or 7BB, rather than to use  $E$  of equation 7A. The isotopic composition has been estimated from the results of positive-ray analysis combined with the chemical atomic weights. *The value for mercury has been calculated from experimental data obtained by the evaporation method.* The coefficient  $B$  or  $B'$  is the value of  $-\Delta^\circ M$ , or of  $\Delta M$  when  $\ln C=1$ , where  $M$  is in general the molecular weight. In the case of molecules, such as that of chlorine,  $\text{Cl}_2$  or carbon tetrachloride,  $\text{CCl}_4$ , containing more than one atom of an isotopic element,  $\Delta M$  or  $-\Delta^\circ M$  must evidently be divided by the number,  $n$ , of such atoms per molecule, in order to get the change  $\Delta A$  or  $-\Delta^\circ A$ , in the atomic weight of the isotopic element. Hence the coefficient  $B'$  must be divided by  $n$ , in such cases, although this is never necessary for  $B$ . The quantity  $\Delta A/\ln C=B$  or  $B'/n$ , calculated for the usual case of  $c=2$ , will be called the "separation coefficient." It might be considered preferable to calculate the quantity  $\Delta A/A$ , but this has not here been done. The values of  $\Delta A/A$  will of course be much less favorable to the heavier elements than are the "separation coefficients" given on the opposite page.

The diffusion or separation coefficient for a given isotopic mixture is proportional to the increase of atomic weight for a definite cut. Since the coefficients ( $B/n$ ) in the table below are calculated from the initial composition of the isotopic mixture, they represent the rate of increase of the atomic weight at the beginning of the diffusion. If neon and hydrogen chloride, for example, are compared it is found that the latter has the higher separation coefficient. If the approximate equation

$$\Delta M = \frac{(M_2 - M_1)^2 x_1 x_2}{c M_1} \ln C$$

is considered, it is seen that  $(M_2 - M_1)^2$  is the same for both of these elements, while the molecular weights give a factor of  $\frac{36.46}{20.20}$  or 1.805 in favor of the neon. However, the product of the mol fractions is 0.0900 for

TABLE I

## COMPOSITION AND SEPARATION COEFFICIENTS OF ISOTOPIC MIXTURES

Element or compound	At. wt. or mol. wt.	At. or mol. wts. of isotopes	Corresponding mol-percentages	$1-k_2$	$B$ or $B'/n_e$	$E$ or $E'/n_e$
Li	6.94	6,7	6,94	0.0742	0.00450	0.00403
B	10.9	10,11	10,90	0.0466	0.00438	0.00409
BH <sub>3</sub>	13.9	13,14	10,90	0.0364	0.00339	0.00322
Ne	20.2	20,22	90,10	0.0466	0.00843	0.00818
Mg	24.32	24,25,26	79,10,11(?)	.....	0.00868	0.00843
HCl	36.46	36,38	77,23	0.02668	0.00950	0.00932
CH <sub>3</sub> Cl	50.46	50,52	77,23	0.01941	0.00690	0.00681
Cl <sub>2</sub>	70.92	70,72,74	59.3,35.4,5.3	.....	0.00494	0.00499
CH <sub>2</sub> Cl <sub>2</sub>	84.92	84,86,88	59.3,35.4,5.3	.....	0.00413	0.00417
CHCl <sub>3</sub>	119.38	118,120,122, 124	45.7,40.9,12.2,1.2	.....	0.00295	0.00296
CCl <sub>4</sub>	153.84	152,154,156, 158,160	35.2,42.0,18.8,3.7,0.3	.....	0.00229	0.00231
Ni	58.68	58,60	66,34	0.01680	0.00758	0.00747
Ni(CO) <sub>4</sub>	170.68	170,172	66,34	0.00582	0.00262	0.00260
Zn	65.37	64,66,68,70	51.5,31,15,2.5(?)	.....	.....	0.02037
K	39.10	39,41	95,5	.....	.....	0.00232
Rb	85.45	85,87	77.5,22.5	.....	.....	0.00409
Kr	82.92	78,80,82,83, 84,86	6,15,18,16, 25,30	.....	.....	0.0306
HBr	80.92	80,82	54,46	0.01228	0.00614	0.00606
Hg	200.6	197-200,202,204	.....	.....	0.0057	(experimental)

neon and 0.1771 for hydrogen chloride, thus giving a factor equal to 1.970 in favor of hydrogen chloride. Though the initial diffusion coefficient is thus more favorable in the case of hydrogen chloride, if an extensive series of diffusions is carried out, it is found that in the case of the *heavy fraction* the diffusion coefficient for both substances increases as the diffusion proceeds, but much more rapidly for neon, so the diffusion coefficient of the latter soon becomes the larger. However, with the *light fraction* the diffusion coefficients of both become less favorable, and that of neon becomes less favorable even more rapidly than that of hydrogen chloride.

The compounds of chlorine listed in the table indicate that if Cl, Cl<sub>2</sub>, Cl<sub>3</sub>, and Cl<sub>4</sub> could be diffused, the rates of separation in terms of the change of atomic weight (separation coefficient) would be respectively 1,  $1/3$ ,  $1/3$ , and  $1/4$ . The values given in the table are slightly different from what would be expected from these ratios, since all but Cl<sub>2</sub> are loaded with either hydrogen or carbon.

The highest rate of separation for an *element* of given isotopic composition is that for monatomic molecules of the pure element. The separation coefficient  $B/n_e$  is very nearly inversely proportional to the total molecular weight (see table), whether the molecule contains one or more atoms of the isotopic element. When  $n_e$  is greater than 1, the mixing of isotopes



in a single molecule tends to reduce the separation coefficients, as pointed out by Harkins in connection with molecular chlorine. This is, however balanced by the effect of the large difference in molecular weight of the lightest and heaviest molecular isotopes, so that the effect of the total molecular weight, as indicated by Equations 7A and 7A', is alone effective. For the separation of the element chlorine, hydrogen chloride is evidently the most favorable compound. The separation coefficient of mercury is rather low, but this is more than compensated, from the experimental standpoint, by the chemical inactivity, volatility and ease of purification of the element, and the accuracy with which changes in atomic weight can be determined by density measurements. According to the theory of Harkins,<sup>20</sup> many or most of the *even-numbered elements* above nickel should contain numerous isotopes. In agreement with this, Aston has found 6 or 7 isotopes each for the elements krypton, xenon, and mercury. The wide separation of the extreme atomic weights tends to give such elements a large separation coefficient, if the extreme components are present in any considerable proportion, for the coefficient depends on the squares of the intervals in atomic weight between isotopes (see Equation 7A').

Such elements as selenium, cadmium, tin, and tellurium, should on this basis, and in the absence of specific information as to the isotopic composition be favorable cases for separation. Experiments upon zinc and cadmium have been begun in this laboratory.

For elements or compounds containing more than two isotopes, it is possible to calculate from the coefficient  $E$  a virtual atomic or molecular weight interval corresponding to the case of only two isotopes. For example, the mixture of isotopes in mercury is equivalent to an equimolal mixture of two isotopes having an atomic weight difference of 3.0 units.

This is obtained by putting  $\frac{(\Delta M)^2 x_1 x_2}{2M} = E = 0.0057$ , setting  $x_1 = x_2 = 0.50$ ,

and solving for  $\Delta M$ :  $(\Delta M)_e = \sqrt{8EM}$ . For magnesium,  $(\Delta M)_e = 1.32$ ; for hydrogen chloride, 1.68; for chlorine, 2.44; for carbon tetrachloride, 3.4; for zinc, 3.3, etc.

### Isotopic Molecules and Isomeric Molecular Isotopes.

The mol-fractions of the various molecular species of a given chemical formula, in the table preceding have been calculated by assuming the molecules to have been built up from their atoms according to chance.<sup>21</sup> If an element containing mol-fractions  $x_1$  and  $x_2$  of two isotopes is combined into molecules containing  $n_e$  atoms each of this element, there will be  $n_e + 1$

<sup>20</sup> Harkins, *THIS JOURNAL*, 37, 1367 (1915).

<sup>21</sup> Soddy (*Nature*, 105, 516 and 642 (1920)) gives the formula for the relative proportions of the isotopes of the chlorine molecule, whose existence had been pointed out previously by Harkins (*Science*, Ref. 1).

isotopic molecular species, whose mol-fractions can be shown to be given by the successive terms of the expansion of  $(x_1+x_2)^{n_s}$ . If the element has ( $s$ ) instead of only two isotopes, the corresponding expression is

$(x_1+x_2+\dots+x_s)^{n_s}$ , which gives  $\frac{(n_s+s-1)!}{n_s!(s-1)!}$  terms, corresponding

to an equal number of molecular isotopes. If the compound contains atoms of several elements  $E, E', E'', \dots$ , each having a set of isotopes, as  $E_1, E_2, \dots, E_s$ , for element  $E$ ;  $E'_1, E'_2, \dots, E'_{s'}$ , for element  $E'$ ; etc., and if each element contains mol-fractions  $x_1, x_2, \dots, x_s; x'_1, x'_2, \dots, x'_{s'}$ , etc., of its isotopic atomic species, then the mol-fractions of the various possible molecular species will be given<sup>22</sup> by the terms of the complete expansion of  $(x_1+x_2+\dots+x_s)^{n_s} (x'_1+x'_2+\dots+x'_{s'})^{n'_{s'}} (\dots)$  ( $\dots$ ).... The total number of terms, and so of molecular isotopes,

is  $\frac{(n_s+s-1)! (n'_{s'}+s'-1)! (\dots) (\dots) (\dots)}{n_s! n'_{s'}! \dots (s-1)! (s'-1)! (\dots) (\dots) \dots}$ . The composi-

tion of the molecular species to which any term refers is given by the particular  $x$ 's occurring in that term, and their exponents. Thus  $(x_1) (x_2) (x'_1) (x'_2) (x'_3)$  would be the mol-fraction of the molecular species  $E_1 E_2 E'_1 E'_2 (E'_3)_1$ . This might represent, for example, one of the isotopes of  $K_2PtCl_6$ , as  $K^{39}K^{41}Pt^{198}(Cl^{35})_2(Cl^{37})_4$ . The number of isotopes of  $K_2PtCl_6$ , if potassium has 2, platinum 6, and chlorine 2, is given by the formula above as  $\frac{3!6!7!}{2!6!1!1!1!5!1!1!} = \frac{3!7!}{2!5!} = 126$ . If tin has 6, and silicon 3

isotopes, then there are 30 molecular species of the formula  $SnCl_4$ , 54 of the formula  $SnCl_2Br_2$ , and 42 of the formula  $Si_2Cl_6$ . If mercury has 6 isotopes,  $Hg_2Cl_2$  has 63 isotopes under conditions where its molecules exist as individuals.<sup>23</sup> Similarly,  $ZnCl_2$  should have 12 isotopes.

Among compounds containing more than one isotopic element, there will often be instances of isotopes of equal molecular weight. For example,  $MgCl_2$ , under conditions<sup>23</sup> where its molecules exist as permanent entities, would contain 9 isotopes having molecular weights 94, 95, 96, 96, 97, 98, 98, 99, 100. For both  $Mg^{24}Cl^{35}Cl^{37}$  and  $Mg^{26}(Cl^{35})_2$  the molecular weight is 96, and for both  $Mg^{24}(Cl^{37})_2$  and  $Mg^{26}Cl^{35}Cl^{37}$  it is 98 (isobaric molecules).

When an isotopic element appears in an organic molecule, its isotopism not only results in numerous isotopic molecular species, but also in many cases introduces new position isomers. For example,  $C_6Cl_6$  must have 7 molecular isotopes, of which all but  $C_6(Cl^{35})_6$  and  $C_6(Cl^{37})_6$  must exist in sev-

<sup>22</sup> These expressions take account of all elements present in a compound, even if some of them contain only one isotope ( $s=1$ ). The factor  $\frac{(n_s+s-1)!}{n_s!(s-1)!}$  reduces to 1 in the latter case ( $0!=1$ , by definition), so that it is necessary to consider only the elements in the molecule which contain isotopes.

<sup>23</sup> I. e., in the vapor state, or in solution in non-ionizing solvents.

eral isomeric forms, due to the presence of the two different substituents  $\text{Cl}^{35}$  and  $\text{Cl}^{37}$ . Again,  $\text{CH}_3\text{CHClCH}_2\text{Cl}$  must consist of 4 molecular species, the isotopes  $\text{CH}_3\text{CHCl}^{35}\text{CH}_2\text{Cl}^{35}$ ,  $\text{CH}_3\text{CHCl}^{37}\text{CH}_2\text{Cl}^{37}$ ,  $\text{CH}_3\text{-CHCl}^{35}\text{CH}_2\text{Cl}^{37}$ , and  $\text{CH}_3\text{CHCl}^{37}\text{CH}_2\text{Cl}^{35}$ , the last two being isomeric forms of the same isotope.

New optical isomers are possible as a result of isotopism, if isotopic atoms, by virtue of their different *masses* alone, can act as different substituents to make carbon or other atoms asymmetric.

### Experimental Work with Mercury.

**Purification.**—The mercury used was purified by prolonged agitation with nitric acid, followed by 5 distillations in a current of air at low pressure according to the method of Hulett and Minchin,<sup>24</sup> who claim that a single distillation gives a completely pure product. The first and last portions were rejected in each distillation, and a final distillation *in vacuo* was made.

**Evaporator.**—The apparatus used in most of the runs was of Pyrex glass. It is shown in Fig. 2. The mercury was placed in the small basin B and was heated from

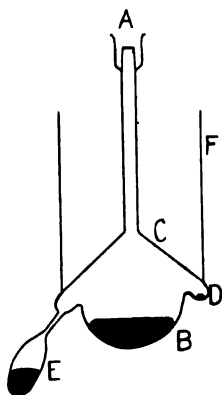


Fig. 2.

Cross-section of evaporator for the separation of isotopes (less efficient form).

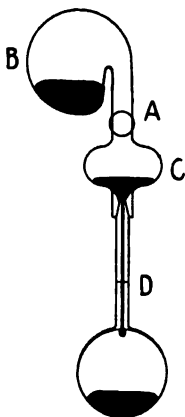


Fig. 3.—Pycnometer.

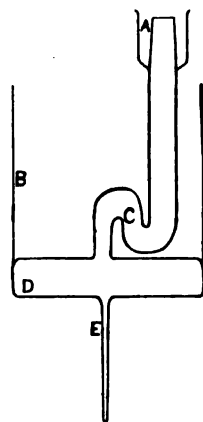


Fig. 4.—Section of efficient evaporator for the separation of isotopes.

below. Ice placed in the cylindrical jacket F caused the evaporating molecules to condense on the roof C whose slope was just sufficient so that the droplets ran down into the annular catch D, thence into the receiver E. The apparatus was filled through A and emptied by cutting off E, containing the condensate, and then pouring the residue out through the opening. The ground-glass joint A was connected to a mercury diffusion pump and oil pump, and to a McLeod gage. During the runs the apparatus was evacuated to a pressure of  $10^{-4}$  to  $10^{-5}$  mm. The efficiency was probably not much reduced until the pressure rose to about  $10^{-3}$  mm., when the presence of air caused a

<sup>24</sup> Hulett and Minchin, *Phys. Rev.*, 21, 388 (1905).

considerable slowing up of the operation, and deflection of the mercury molecules so that some of them condensed on the roof of D.

The first runs were made with the form of apparatus shown in Fig. 4, which had the evaporating and condensing surfaces very close together, so that a high efficiency was to be expected. About 1000 g. of mercury was sucked into the apparatus at the beginning of the run, through the narrow tube at the bottom, which was then sealed off. The bottom of the apparatus was heated by a hot water bath fitted around it, and the evaporating molecules were condensed in the form of a solid on the roof of the apparatus, by the use of a mixture of solid carbon dioxide and toluene contained in an insulated cylindrical jacket fitted over the roof. After a run, air was admitted, and the residual liquid mercury allowed to run out through the tube at the bottom, which was cut open. The solid condensed mercury, after it had melted, was allowed to run out through the same opening. The use of this efficient form of apparatus had to be given up on account of the expense involved in supplying the necessary carbon dioxide or liquid air.

**Pycnometer.**—A special form of pycnometer was used in the density determinations. The pycnometer proper consisted of a glass bulb sealed to a thermometer capillary. This was fitted by means of a ground-glass joint to a filling device (Fig. 3). This consisted of two bulbs, and a side-tube A with a third bulb and a ground-glass joint through which the apparatus was evacuated. The mercury sample was placed in the upper bulb B and by rotating A, was caused to flow into the lower bulb C after the pycnometer was evacuated. Air was then admitted into the bulbs, which forced the mercury into the pycnometer. By filling at a low temperature, and then letting the mercury overflow at a suitable determined temperature, the meniscus was brought approximately to the mark (D) at 25.000°. Its distance from the mark was then measured by means of a cathetometer, and the observed weight of the filled pycnometer corrected accordingly. The correction was seldom over 0.1 mg. For a given sample in the same pycnometer, the corrected weights in successive fillings practically never varied among themselves by more than 0.3 mg., the extreme variation averaging about 0.2 mg., even when the weighings were made at intervals of days or weeks. The mean of three or more refillings was certainly correct to better than 0.1 mg. or about 1 part in 1,000,000, as can be judged from the table below. Two pycnometers were used in the determinations, one weighing when empty 13.4721 g. and holding 72.6375 g. of ordinary mercury, the other weighing 20.6576 g. and holding 106.9962 g. The air-buoyancy correction for the filled pycnometer was only 0.56 mg. in the first case and 0.95 mg. in the second, and therefore not appreciably dependent on the atmospheric density. The effects of pressure on the thermometer (0.002° per cm. of mercury), and on the pycnometers were also too small to require a correction, especially in view of the fact that the atmospheric pressure varied only from 741 mm. to 751 mm. during the whole series of determinations. No attempt other than filling the pycnometer at very low pressures was made to free the samples from dissolved gases, but this factor affected all the samples alike.

**Results.**—With a cut of 1.03, using the apparatus of Fig. 4, the combined condensates (Sample 1 of table p. 61) from two short runs showed a density 29 parts in 1,000,000 less than that of the original material. By Equation 7', this gives the value 0.0057 for the "separation coefficient" ( $B'$ ) of mercury. Brönsted and von Hevesy reported an increase of density of 31 parts per million for the residue for a cut of about 4, and a decrease of 20 parts per million for the condensate for a cut of about  $\frac{7}{6}$ . The average value of  $B'$  calculated from these data is 0.0042, so that their efficiency was about 75% assuming the above value of  $B'$  to correspond

to 100% efficiency. In the table below, the results of the present work are summarized. The same sample of pure mercury was used throughout as a standard of density and differences from this standard are expressed in parts per million. Using the apparatus of Fig. 2, which had an (initial) evaporating area of 17 sq. cm., and evaporating at a rate of 1 g. per sq. cm. per hour, at 40°, an efficiency of 93% was obtained (Sample 2 of table). In a run at 85°, with an evaporation rate of 2.6 g. per sq. cm. per hour, an efficiency of 83% was obtained (Sample 3).<sup>21</sup> After making these short runs, a systematic fractionation was undertaken, using successive cuts of 2. It was aimed to sacrifice efficiency somewhat to speed in the earlier stage, so that, allowing for various accidental causes of inefficiency, an efficiency of 80% was expected. One hundred and fifty g. of a light fraction (Sample 4) resulting from four successive cuts of 2, has been obtained, and shows a *decrease of density of 64 parts per million*, in exact agreement with that calculated for an average efficiency of 80% in each operation. Similarly, by making four cuts of somewhat more than 2, or a total cut of about 20 or 25, 140 g. of a heavy fraction (Sample 5) has been obtained which shows an *increase in density of 69 parts per million*, again completely in agreement with that calculated. A larger separation could undoubtedly have been obtained but the above results were considered convincing. Further work is being done on the separation of the isotopes of mercury by evaporation and diffusion methods.

Some of the purified mercury used in the above evaporations was subjected to distillation under reduced pressure, with the intention of showing the absence of impurities. The only possible impurities which could have been present are all much less volatile than mercury, and so should have become concentrated in the residue, if not wholly oxidized during the preliminary treatment, or by the air during the distillations. Most of these impurities (zinc, cadmium, lead, iron, etc.) are decidedly less dense than mercury, so that their presence in the residue would cause a decrease in its density. Only the very slightly volatile metals like platinum, gold, etc., which could not possibly be present in appreciable amount after the several redistillations, could have caused an increase in density. Actually, in every case, the residue from a distillation was found denser (4 to 7 parts per million) than the original material; and the first portion of distillate was if anything slightly less dense. While this cannot be accounted for by the presence of impurities, (unless by the presence of an undiscovered element similar to mercury, but denser and just a little less volatile) it is perfectly satisfactorily explained as due to a very inefficient separation

<sup>21</sup> For a perfectly clean surface (see Knudsen, *Ann. Phys.*, 47, 697 (1915)); this rate of evaporation (2.6 g.) should be reached at 54°, while at 85° the rate should be about 19 g./sq. cm./hr., according to the Hertz formula. The *relative* rate of evaporation of isotopes should not be affected, however, by the reduced *total* rate of evaporation.

of isotopes as a result of incomplete equilibrium during the vaporization of the mercury. The relatively large changes of density of the residues, as compared with the distillates, are in harmony with the theory. The cut is very large (about 12) for the residues, thus producing a relatively large *increase* in density, while the corresponding *decrease* for the first fraction of distillate should be numerically equal (see theoretical discussion) to the increase for a cut of 2.7. The efficiency of the distillations, as compared with the method of evaporation, was about 6% for Sample 6, which was distilled rapidly, and about 10% for Sample 7, which was distilled slowly. Evidently there is a slight separation of isotopes every time mercury is distilled under reduced pressure. In fact, a similar effect must occur, to an extent usually negligibly slight, indeed, in every distillation of substances containing isotopes.

Aside from the indication of a slight separation of isotopes, the results of the distillations, in which conditions are as favorable as possible for impurities to show their presence, show conclusively that the changes of density resulting from the evaporations, which are made under conditions distinctly unfavorable to a separation of impurities, yet yield changes of density of a larger *order of magnitude* than the distillations, must be due to a separation of isotopes.

The results show that even a considerable number of collisions of molecules can occur before condensation without great loss of efficiency. The instantaneous molecular density in the space above the evaporating liquid should, according to calculations, be about  $\frac{1}{3}$  that in the saturated vapor if no collisions occur. The vapor pressure corresponding to an

TABLE II  
SUMMARY OF DENSITY RESULTS  
Density Changes in Parts per Million

*Evaporations*

Sample	Cut	No. of Mean change refillings of density of pycnometer	(p. p. m.)	Av. deviation (a.d.) of mean (p. p. m.)
1 Condensate.....	1.03	2	-29	$\pm 0.7$
2 Condensate.....	....	3	-20	0.4
Residue.....	2.22	2	+18	0.2
3 Condensate.....	....	2	-20	0.1
Residue.....	1.57	1	+ 9	...
4 Light fraction.....	4 cuts of 2	2	-64	0.7
5 Heavy fraction.....	20 or 25	2	+69	

*Difference in Density Between Extreme Fractions, 133 Parts per Million.*

*Distillations*

6 First fraction.....	....	2	-1.5	$\pm 1.6$
Residue.....	(?)	2	+3.5	0.4
7 First fraction.....	....	..	.....	...
Residue.....	11.9	2	+4.0	0.8
8 First fraction.....	(6 cc. out of 85 cc.)	3	-1.5	0.9
Residue.....	13.0	3	+7.2	0.8

evaporation rate of 4 g. per sq. cm. per second is 0.025 mm., and the mean free path in saturated vapor at this pressure is about 1 mm. The actual mean free path was probably not over 3 mm. The average net distance any molecule had to travel before condensation was about 30 mm. in the apparatus used,<sup>26</sup> so that every molecule must have suffered a number of collisions on its way.

### A Classification of Methods used for Separating Isotopes.

It seems worth while to classify, in outline form, the principal methods which might be used for separating isotopes.<sup>27</sup>

- I. Methods using phenomena involving thermal motion of molecules and dependent on molecular velocities and their distribution. Separation necessarily incomplete.
  1. Equilibrium practically complete,<sup>28</sup>—pressure and temperature constant throughout the system,—little or no separation.<sup>29</sup>
    - A. Slow distillation, slow crystallization, chemical reactions in general.
  2. Equilibrium under a pressure or temperature gradient,<sup>30</sup>—degree of separation proportional to logarithm of ratio of pressures or temperatures at ends of gradient, which ratio may theoretically be made indefinitely great, but practically is limited.
    - A. Equilibrium under a pressure gradient, due to gravity or rapid rotation,<sup>37</sup> or electron impact,<sup>31</sup> etc.,—degree of separation proportional to the logarithm of the pressure ratio; or for centrifugal separation, to the square of the peripheral velocity, also to the product of the mol fractions and to the square of the interval between the atomic weights of the two isotopes, but *independent of the molecular weight*.
    - B. Equilibrium under a temperature gradient (thermal diffusion<sup>32</sup>)—degree of separation approximately proportional to the logarithm of the temperature ratio; also to the product of the mol fractions, to the square of the difference of the molecular weights of the two isotopes, and *inversely proportional to the molecular weight*.
  3. Non-equilibrium processes. Flow under a gradient of partial pressure or concentration. The maximum efficiency of separation in A, B, and C, is given for zero partial pressure at the lower end of the gradient. The degree of separation in A, B, and C, is definite and limited for the light fraction, but proportional to

<sup>26</sup> In the more ideal apparatus shown in Fig. 4 this distance could be made as little as 5 mm. This apparatus was found to have a higher efficiency than that illustrated in Fig. 2. The use of the less efficient form as in the present work, is not advisable, since, in order to produce a given amount of material having a given change in atomic weight a multiplication of the number of operations is necessary.

<sup>27</sup> Compare Lindemann and Aston, *Phil. Mag.*, [6] 37, 523 (1919), who discuss in particular, methods I, 1; I, 2, A; and II, 1.

<sup>28</sup> Compare Lindemann and Aston, Ref. 27; Lindemann, *Phil. Mag.*, [6] 38, 173 (1919); Soddy, Ref. 21.

<sup>29</sup> A photochemical method of separation is being tried by Merton and Hartley (*Nature*, 105, 104 (1920)).

<sup>30</sup> A fuller discussion of these methods of separating isotopes, including a comparison with the diffusion methods here discussed, will be given in a subsequent paper.

<sup>31</sup> Skaupy, *Z. Physik*, 2, 213 (1920).

<sup>32</sup> Chapman, *Phil Mag.*, [6] 38, 182 (1919).

the logarithm of the cut for the heavy fraction; while for both fractions it is proportional to the product of the mol fractions (as in thermal diffusion).

- A. Molecular effusion and non-equilibrium evaporation.<sup>33</sup>
- B. Molecular diffusion.
- C. Interdiffusion of gases.
- D. Liquid diffusion (separation probably small because diffusion coefficients in liquids depend on atomic or molecular volumes).
- E. Rapid solution, precipitation, etc.<sup>34</sup>
- F. Initial effects in evaporation, diffusion, etc.
- II. Methods using phenomena in which molecules act as independent masses,—separation almost complete.
  1. Positive ray methods,<sup>37</sup>—yields very small, though products are, theoretically, almost pure.
  2. Possibly, electrolysis of ionized liquid or gas (separation probably difficult or impossible, because mobility of isotopic ions is probably practically equal; slight differences of mobility will be masked by diffusion and convection).<sup>34</sup>

### Summary.

1. The various phenomena of diffusion and effusion in gases are discussed in connection with the separation of isotopes. (a) It is shown that for the processes of molecular diffusion through a porous membrane, molecular effusion, and non-equilibrium evaporation, the relative rates of escape of isotopes are proportional to their respective mol-fractions and inversely proportional to the square roots of their molecular weights. In all the above processes the molecules (which may of course be monatomic, as in the case of neon or mercury) move independently. As collisions between molecules become more frequent, molecular diffusion passes into capillary transpiration, or mass motion, and non-equilibrium evaporation passes into ordinary distillation. In either case, practically no separation of isotopes occurs. (b) If a gaseous mixture of isotopes diffuses into another gas, with no convective mixing, the diffusion coefficients of any two isotopes are probably in the ratio  $\frac{x_1}{x_2} \sqrt{\frac{M_2}{M_1}}$ , where  $c$  is a variable quantity

usually in the neighborhood of 1 or 2. The theory is complicated, but indicates a higher rate of separation than for molecular diffusion and evaporation, for which  $c$  is always 2. (c) Another possible method is that of "initial diffusion," which would take advantage of the fact that the front

<sup>33</sup> The method of irreversible condensation of a vapor or gas is a special case of the method of molecular effusion, and is thus somewhat similar to irreversible evaporation. J. J. Thomson's suggestion (*Proc. Roy. Soc.* 99A, 87 (1921) that the isotopes of chlorine might be separated by fractional absorption of hydrogen chloride in an alkaline solution would make use of this method. This would hardly be practical, however, due to the rapidity of the absorption and the consequent impossibility of good mixing. If air were admixed with the hydrogen chloride, there might be some degree of separation as a result of gaseous diffusion.

<sup>34</sup> See also Lindemann, *Proc. Roy. Soc.* 99A, 87 (1921).



rank of molecules diffusing into a gas or a vacuum should be enriched in the lighter isotopes.

2. The theory of non-equilibrium evaporation is discussed. If the vapor pressures of isotopes when pure are equal, a separation *must* occur when an isotopic liquid is evaporated *in vacuo* in such a way that practically all the evaporating molecules are condensed. For an efficient separation good mixing must take place in the surface and body of the liquid. This consideration bars the use of the method with solids, but solutions or liquid alloys might be used.

3. Simple and closely approximate equations are developed for the change in the mol-fraction of any isotope and for the change of atomic weight in a mixture of any number of isotopes, when the latter is separated into fractions by a diffusion or evaporation process. (See Equations 6 to 16 and 6' to 16'). These hold closely only for small changes in atomic weight, but by a second approximation, Equations 8, 9, 10, 17, 18 are obtained, which hold closely even for changes of considerable magnitude, Equations 3 and 4 permit exact calculations in the case of large changes, but apply only to the case of two isotopes. *The rate of separation of two isotopes, as measured by the change in atomic weight for a given operation is proportional to the square of the interval between the molecular weights of the two isotopes, inversely proportional to the ordinary molecular weight, and proportional to the product of the mol-fractions of the isotopes.* For a mixture of any number of isotopes, similar relations are shown to hold. For a given element, the *separation coefficient* (equal to the decrease of atomic weight of the isotopic mixture for the first small portion of diffusate or condensate) *is inversely proportional to the molecular weight of the compound in which that element is combined.* A table of separation coefficients is given, calculated from atomic weights and the results of positive ray analysis. The value given for mercury has been calculated from the present experimental data.

4. Most of the equations developed apply to the separation by diffusion of any gaseous mixture, whether or not it consists of isotopes. Equations 3, 4, 9, 10, 6, 7, 6B, and 7B are especially useful. Equations 6A, 6A', 7A, and 7A', are applicable only to the separation of a mixture of gases having very nearly the same molecular weight; Equations 6B and 7B fail only if the ratio of molecular weights is far from unity.

5. In systematic fractionation the diffusate (or condensate) being formed at any time has an atomic weight less than that of the corresponding residue, which becomes denser as the diffusion proceeds, by a constant amount. *Thus the enrichment of the light fraction is a maximum at the beginning. The atomic weight of the residue increases indefinitely, however, in proportion as the logarithm of its quantity decreases, while at the same time the atomic weight of the total diffusate approaches that of the original*

material. (Consult Fig. 1). The use of cuts of 2 gives equal and opposite enrichments for the two fractions, equal in magnitude to 0.693 times the separation coefficient, or initial enrichment for the light fraction. Efficiency conditions are discussed.

6. Formulas are given for calculating the proportions and numbers of isotopic molecular species in compounds containing several isotopic atomic species. Zinc chloride contains 12 molecular isotopes, and if, for example, tin has 6 isotopes, the compound  $\text{SnCl}_4$  is a mixture of 30, and  $\text{SnCl}_2\text{Br}_2$ , of 54, different molecular isotopes. The existence of many new isomers due to isotopism is also pointed out.

7. Experimental work on the partial separation of mercury into isotopes by non-equilibrium evaporation is described.<sup>25</sup> Calculation based on data for a very efficient evaporation gives a value of 0.0057 for the separation coefficient of mercury. Other runs with a less efficient apparatus gave concordant data. The results agree with those reported by Brönsted and von Hevesy, but the efficiency is better than theirs. By making four successive cuts of approximately 2, on both light and heavy fractions, a much larger decrease, of 64 parts per million, or 0.013 units of atomic weight, has been obtained on the lightest fraction, and a corresponding increase of 69 parts per million or 0.014 units on the extreme heavy fraction. The results are in complete agreement with the theory developed in this paper. *The total difference in density between the extreme fractions is thus 133 parts per million, and the difference in atomic weight, 0.027 units.* Data are given showing that a slight separation of isotopes occurs even in an ordinary distillation under reduced pressure.

8. A classification in outline of the possible methods for separating isotopes is given.

#### CHICAGO, ILLINOIS.

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<sup>25</sup> A larger separation has very recently been obtained by molecular diffusion of mercury vapor through filter paper at 150°. The results indicate that the separation coefficient of mercury is higher than 0.0057. A chemical method of separation and an electrolytic method have also been tried. All these will be described in a later paper.

[CONTRIBUTION FROM THE SEVERANCE LABORATORY OF OBERLIN COLLEGE.]

**CELLULOSE NITRATE AS AN EMULSIFYING AGENT.**

BY HARRY N. HOLMES AND DON H. CAMERON.

Received September 8, 1921.

Two immiscible liquids are readily emulsified temporarily by shaking, but a third substance, the so-called "emulsifying agent" must be present to insure stability to the emulsion. Soaps are the best known emulsifying agents, but other substances are used, even gelatin and basic cupric sulfate. As a general rule the emulsifying agent must be soluble in, or rather, peptized by one of the liquids. This explains the common use of colloids for this purpose, yet a finely divided substance that is more readily wetted by the one liquid than by the other may serve.

Cellulose nitrate is colloiddally dispersed in such a number of liquids that it seemed certain it must be an excellent emulsifying agent for certain pairs of immiscible liquids. In addition, its use promised to throw some light on the various theories of emulsification. Schoepf<sup>1</sup> used it to emulsify glycerol in alcohol-ether.

**Choice of Liquids.**—Water is generally selected as one of the two liquids in an emulsion but glycerol may be used in its place in most cases. Pairs of immiscible liquids that do not use either water or glycerol are far from numerous. In the conventional phrases "water-in-oil" or "oil-in-water" emulsions we class water and glycerol as "water," and most other liquids as "oil."

For this research, the liquids chosen are arranged in pairs. Liquids under *A* are insoluble or but slightly soluble in the liquids under *B*. Their action toward cellulose nitrate is indicated. Cellulose nitrate is abbreviated as "c. n."

A			- B
Do not peptize c. n.	Peptize c. n.	Indifferent	Precipitate c. n.
Glycerol	Acetone	Benzene	Carbon disulfide
		Toluene	Carbon tetrachloride
			Chloroform
Glycerol	Ethyl acetate	Toluene	Chloroform
or	or		
Water	Amyl acetate	Toluene	

**Peptization of Cellulose Nitrate.**—Cellulose nitrate is peptized by acetone, amyl acetate, alcohol-ether, acetic acid, etc. From such solutions it is readily precipitated by any liquid which does not peptize it and which is soluble in the given cellulose-nitrate solvent. For example, carbon disulfide, carbon tetrachloride and chloroform precipitate the nitrate from "solution" in amyl acetate. Water will precipitate it from water-soluble solvents such as acetone, methyl alcohol and acetic acid.

<sup>1</sup> *Kolloid Z.*, 8, 83 (1911).

Benzene and toluene, while they do not peptize the dry ester, can be added in large amounts to solutions of that material in other solvents, without causing precipitation. Possibly these two liquids possess some peptizing power.

**Emulsion Types.**—Using cellulose nitrate as the emulsifying agent, the emulsions formed were of the "water-in-oil" type. For example, emulsions of water in amyl acetate and of glycerol in acetone were formed. The type was determined by placing a drop of the emulsion upon the liquid of each phase and observing with which liquid it was miscible. An emulsion of water in amyl acetate mixed readily with amyl acetate, indicating that water was the dispersed phase.

**Theory of Emulsification.**—Cellulose nitrate, peptized in a mixture of 1 part of amyl acetate and 3 parts of benzene, will form the continuous phase for an emulsion with water as dispersed phase. If several large drops of water are added to such a cellulose nitrate solution in a beaker, a film can soon be seen to form around each water drop. These films appear to be of a tough and elastic nature and to interfere with the coalescence of the drops. This is visible evidence to support the theory that a coherent film of the colloidal emulsifying agent is formed around each dispersed drop in an emulsion.

The film which is formed in this case is rendered visible when there is sufficient difference in refractive index between the film and the surrounding liquids. In other emulsions the film may be present but invisible because there may be no such difference in refractive indices.

A visible interfacial film indicates an increased concentration of the emulsifying agent at the liquid-liquid interface. This increase was determined quantitatively in the manner described below.

### Experimental Part.

An emulsion of glycerol dispersed in an acetone solution of cellulose nitrate was selected for this study. This system is one in which water is not used for either phase. Both phases readily dissolve in water while the emulsifying agent remains undissolved.

**Reagents.**—The glycerol used was a commercial U. S. P. IX quality. The index of refraction of this was observed and found to be 1.4668 at 20°, indicating the presence of about 4–5% of water.

The acetone was a commercial c. p. grade which had been dried for several days over calcium chloride and further purified by distilling over calcium chloride.

A sample of cellulose nitrate<sup>2</sup> containing 11.04% of nitrogen was selected for this work. The solid ester was dried in the air over a steam radiator for several days and a 5% stock solution prepared by peptizing in acetone.

**Procedure.**—Acetone was found to be somewhat soluble in glycerol, so the glycerol for the dispersed phase was first saturated with acetone.

<sup>2</sup> Obtained through the courtesy of the E. I. Du Pont de Nemours Co.

Seven cellulose nitrate-acetone solutions were prepared from the stock solution, each with a different concentration of the nitrate. These solutions were used for the continuous phase in a set of emulsions prepared as follows.

Twenty-five cc. of cellulose nitrate-acetone solution was measured with a pipet into a 125cc. emulsion bottle of 35 mm. diameter. Forty cc. of glycerol was added, with 5 minutes' shaking in a power-driven shaking machine after each addition. Twenty-five minutes' additional shaking was given after the final addition of glycerol, in order to produce a maximum and uniform disintegration of the glycerol into minute drops.

The shaking machine was of such a size that 7 of the emulsion bottles could be shaken at one time. A set of 7 emulsions, each with acetone solution of different cellulose nitrate content, was prepared. The 7 emulsions received the same mechanical treatment and were in all ways subjected to uniform conditions.

After being prepared this set was put aside to "cream." In these emulsions, since the glycerol has a greater density than the acetone, the cream layer sinks, leaving a clear acetone-cellulose nitrate solution at the top, with a sharp boundary between the two layers.

After "creaming" had taken place, 10 cc. of the clear acetone layer above was removed and the cellulose nitrate content determined, and compared with that of the original cellulose nitrate-acetone solution.

**Determination of Cellulose Nitrate Content.**—Several different methods were tried and the following finally chosen as a satisfactory means of accurately determining the cellulose nitrate content of an acetone solution. The difficulty encountered in this determination was that of removing the small amount of glycerol retained by the acetone.

Ten cc. of the acetone solution was withdrawn with a pipet, the same pipet being used in each case. This was put into a 100cc. beaker and about 50 cc. of water added, causing some of the nitrate to go into a coarse colloidal suspension while the remainder was precipitated in curdy form. Two drops of a 10% solution of aluminum chloride were then added to coagulate the suspended matter, and the whole heated to boiling for a few minutes to eliminate the acetone and aid coagulation. The precipitated material was then filtered on a weighed Gooch crucible, washed with water and dried to a constant weight at 90-100°. Care was taken to prevent decomposition of the material from overheating. The cellulose nitrate contents of both the stock solution and the solutions from the emulsions were determined in this manner.

**Experimental Results.**—After the set of 7 emulsions had stood undisturbed for 18 hours, 10 cc. of the clear acetone layer was removed and the cellulose nitrate content determined. The exact content in the original solutions was also accurately measured. The values of Table I were observed.

By comparison of the values obtained in Determinations I and II on the stock solutions it is seen that the method gave results accurate to the third decimal place.

TABLE I  
RESULTS

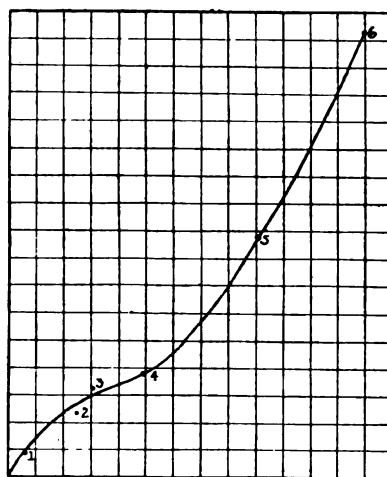
	Stock solution				
	I G.	II G.	Average G.	From emulsion G.	Loss of Ester G.
1	0.0051	0.0064	0.0058	0.0049	0.0009
2	0.0275	0.0273	0.0274	0.0251	0.0023
3	0.0345	0.0342	0.0344	0.0310	0.0034
4	0.0528	0.0533	0.0531	0.0493	0.0037
5	0.0988	0.0988	0.0988	0.0910	0.0078
6	0.1468	0.1458	0.1463	0.1300	0.0163
7	0.2332	0.2498	.....	0.2168	.....

**Speed of Creaming and Stability.**—The speed of creaming and the stability of the emulsions in the above set were progressive from 1 to 7. Emulsion 1 creamed very quickly, and in less than an hour started to break. Emulsion 7 creamed very slowly, and after 18 hours the acetone layer was but little more than 10 cc. in volume. This emulsion—that is, the cream layer in the bottle—did not break for more than a week. Between these extremes the creaming and breaking while progressive as to order, showed some variations in regard to time. Emulsions 1, 2, 3 and 4 were comparatively unstable, breaking in less than 3 days. Emulsions 5, 6 and 7 were of the same order of stability. They remained unbroken for a week.

It will be noted that these emulsions were made with such proportions of the two liquids that a cream of 70 to 80 % dispersed phase could separate, leaving a clear upper layer of about 15 cc. of acetone.

### Conclusions.

The experimental data show that there is an increase in concentration of cellulose nitrate at the acetone-glycerol interface. The values, when plotted, do not give a curve resembling a typical adsorption curve, but rather show some irreversible reaction, as coagulation, in addition to adsorption.



10 20 30 40 50 → c  
Adsorption of cellulose nitrate by glycerol at the acetone-glycerol interface.

a	c
Grams adsorbed in 10 cc.	Grams free in 10 cc.
1. 0.0009	0.0049
2. 0.0023	0.0251
3. 0.0034	0.0310
4. 0.0037	0.0493
5. 0.0078	0.0910
6. 0.0163	0.1300
7. —	0.2168

The nature of the curve is such as would be expected after having seen a visible film of the nitrate form around water drops in an amyl acetate-benzene solution as mentioned above. Between 0 and 4 on the curve there is evidence of adsorption only. Between Points 4 and 5 some radical change occurs and we believe that adsorption is so great that precipitation or coagulation results.

The change in direction of the curve between Points 4 and 5, since it is the result of a sudden increase in the amount of cellulose nitrate at the acetone-glycerol interface, should correspond to some physical difference between Emulsions 4 and 5. As noted above, emulsions 1, 2, 3 and 4 are much less stable than Emulsions 5, 6 and 7.

The values and consequently the curve given cannot be claimed as absolutely accurate although the 7 emulsions were made under the same conditions and subjected to identical treatment. It is assumed, however, that the active surfaces in all the emulsions were very nearly the same.

**The Interfacial Film.**—The stability of any emulsion is due largely to the nature of the interfacial film which is formed. From the above results it seems probable that with cellulose nitrate there is a minimum concentration of the nitrate necessary for the production of a stable emulsion.

The interfacial film may be regarded as an equilibrium product resulting from the precipitating action on the "water" side and the peptizing action on the solvent side. When equilibrium is reached the amount of cellulose nitrate in the film should be in equilibrium with the amount in "solution."

The desirable film for an emulsion is one that forms readily and comes to equilibrium in a short time. It should be elastic, tough, and should change little with age. Such a film on the "solvent" side will be gelatinous and swollen with that liquid, due to peptizing action. On the "water" side, the cellulose nitrate will be coagulated and "wetted" somewhat by the "water" phase.

### Summary.

Cellulose nitrate was found to serve as an excellent emulsifying agent in dispersing water (or glycerol) throughout amyl acetate or other "solvents" for the nitrate.

Visible concentration films of cellulose nitrate were observed around large drops of water "emulsified" in amyl-acetate-benzene. An increase in concentration of cellulose nitrate at the acetone-glycerol interface was studied quantitatively.

The properties of an ideal emulsifying film are discussed.

OBERLIN, OHIO.

[CONTRIBUTION FROM THE SEVERANCE CHEMICAL LABORATORY OF OBERLIN COLLEGE.]

## CHROMATIC EMULSIONS.

BY HARRY N. HOLMES AND DON H. CAMERON.<sup>1</sup>

Received September 8, 1921.

Emulsions exhibiting a wide range of structural colors (suggestive of the chromatic scale of tones in music) were first prepared by Bodroux<sup>2</sup> who, however, neglected to use an emulsifying agent. Consequently his emulsions quickly separated into two layers. Our use of very different liquids with cellulose nitrate as an emulsifying agent enabled us to prepare remarkably beautiful emulsions that lasted for several weeks. We secured these colors in attempting to prepare a number of transparent emulsions.

**Transparent Emulsions.**—Ordinarily when two transparent liquids are emulsified a milky-white mixture results. For example, kerosene shaken with water gives such an emulsion. Yet transparent emulsions can readily be prepared. Transparency depends upon the relative indices of refraction of the two liquid phases. If both phases have the same refractive index, there will be neither reflection nor refraction and the system will appear homogeneous and entirely transparent.

Glycerol and olive oil are mutually insoluble and emulsify on shaking, forming a rather transparent emulsion. A more transparent mixture is obtained by dispersing glycerol in carbon tetrachloride using calcium oleate (previously dissolved in the carbon tetrachloride) as the emulsifying agent.

Glycerol and amyl acetate are mutually insoluble and yield an excellent creamy emulsion on shaking. The same is true of water and amyl acetate. Yet when a mixture of water and glycerol having the same index of refraction as amyl acetate was shaken with the latter liquid a perfectly transparent emulsion was obtained. Cellulose nitrate (11% nitrogen) was dissolved in the amyl acetate as emulsifying agent.

The refractive indices of these liquids as measured by an Abbe refractometer were as follows.

	$n_D^{20}$		$n_D^{20}$
Olive oil (commercial).....	1.4690	Water.....	1.3330
Glycerol (U. S. P.).....	1.4660	Glycerol-water.....	1.4028
Carbon tetrachloride.....	1.4600	Amyl acetate containing 6% of cellulose nitrate.....	1.4045

With the cellulose ester dissolved in amyl acetate the glycerol-water becomes the dispersed phase but with sodium oleate as the emulsifying agent dissolved in the water the phases are reversed—without loss of transparency.

<sup>1</sup> The authors are indebted to Mr. E. Wynne Boyden for valuable laboratory assistance in this research.

<sup>2</sup> Bodroux, *Compt. rend.*, 156, 772 (1913).



Nujol (pure liquid paraffine) containing 2% of crepe rubber when shaken with an equal volume of glycerol yields a very good transparent emulsion. Here the rubber is the emulsifying agent and the glycerol the dispersed phase.

Pulverized cryolite is scarcely visible in water because its index of refraction is nearly the same as that of water.

**Emulsions with Structural Colors.**—In attempting to disperse glycerol in an acetone solution of cellulose nitrate we failed to get transparency. Since the index of refraction of the acetone (1.35886) was lower than that of the glycerol (1.4660) we added benzene (1.50144) cautiously to the milky emulsion in order to equalize the indices of the two liquid phases. Of course the benzene diluted the acetone thus becoming a part of the continuous phase. With cautious additions, and shaking, increased transparency was secured but accompanied by a startling development of colors. At first the emulsion became yellow as viewed from the side and a soft blue when held between the eye and the source of light. With further addition of benzene the yellow changed to beautiful pink while the blue became green. More benzene changed the pink to lavender and later to a peacock-blue. Finally, the emulsion lost color and became milky.

The colors were restored, in reverse order, by cautious additions of acetone.

The explanation of this phenomenon as given by Christiansen<sup>3</sup> and Bodroux<sup>4</sup> was verified by an examination of the Landolt-Börnstein tables of optical dispersive power of liquids. Benzene has more than twice the dispersive power of acetone. Optical dispersion is measured as the difference in the indices of refraction for light of two different wave lengths. In other words, a prism filled with benzene spreads light into a broader spectrum than does a prism filled with acetone. Consequently, drops of one liquid in another of very different optical dispersive power must give the effect of a great number of lenses or prisms with inevitable prismatic color effects.

Transparency is essential in chromatic emulsions for light of some color must pass directly through the emulsion. Yet transparency alone is not sufficient as shown by such emulsions as glycerol in carbon tetrachloride. Thus the selection of liquids for chromatic or structural color emulsions involves two factors: equality of indices of refraction and the

<sup>3</sup> Christiansen (*Wied. Ann.*, 23, 289 (1884)) shook fragments of glass with a mixture of benzol and carbon disulfide. However, the work with emulsions affords a greater variety and far greater beauty than the work with irregular fragments of solids.

<sup>4</sup> Bodroux, Ref. 2, shook a saturated aqueous solution of sodium chloride with ethyl acetate and at a definite temperature found this transient emulsion transparent for light of a definite color. We secure our color change by carefully changing the proportions of the two miscible liquids in the continuous phase. Furthermore, our use of an emulsifying agent gives a definite stability to the emulsions.

greatest possible difference in optical dispersive power. From such values as those in the following table we were able to substitute other liquids for those first used—apparently a sufficient verification of the theory outlined.

I Dispersed phase	Index of refraction	Optical dispersive power
	$^{\circ}\text{C}$	$(n_D - n_C)$ $^{\circ}\text{C}$
Glycerol.....	1.466 —20	0.007 —20
II Continuous phase		
(a) Acetone.....	1.35886—19.4	0.00684—19.4
Amyl acetate.....	1.40170—17.9	0.007 —17.9
(b) Carbon disulfide.....	1.61847—20	0.03210—20
Benzene.....	1.50144—20	0.01664—20
Toluene.....	1.4992 —18.7	0.0160 —14.7
Bromobenzene.....	1.55977—20	0.01923—20
Ethyl bromide.....	1.53806—20	0.01422—20
Benzyl acetate.....	1.50682—17.3	0.01660—17.3

Water may be substituted for glycerol, but the high viscosity of the latter adds to the stability of the emulsions and also to their beauty. It is interesting to invert a tube half filled with a chromatic emulsion and note that the intensity of color in the viscous film is practically as great as in the main body of liquid.

It is necessary to have two mutually soluble liquids for the continuous phase, one of them of high refractive index and high optical dispersive power. On careful addition of this liquid to a milky emulsion already prepared it is possible to change gradually both the refractive index and optical dispersive power. This insures the chromatic range of colors. Carbon disulfide is an excellent liquid to use (except for its offensive odor) because it stands high in both the essential physical properties. There is, however, considerable freedom of choice. The colors change somewhat with change in temperature since there is an unequal temperature effect on the optical dispersive power of the two phases. As Bodroux used only two liquids in each emulsion he was forced to secure his color effects by temperature change.

Cellulose nitrate (11% nitrogen) is an excellent emulsifying agent since it dissolves readily in acetone, amyl acetate and some other liquids, thus forcing the glycerol to become the dispersed phase, as desired. Raw crepe rubber may be substituted for the cellulose ester. For example, a 2% solution of rubber in toluene may be shaken with water which has been saturated with cane sugar to give it high optical dispersive power and high refractive index. Emulsions with a beautiful play of colors are secured. It is convenient to dissolve 20 g. of sugar in 1 g. of water somewhat above  $20^{\circ}$  and then cool. Slight inversion of the sugar with acid prevents crystallization. A trace of gasoline lowers the refractive index of toluene to a suitable point.

Potassium iodide gives water high optical dispersive power and a high index of refraction; so, Nujol may be dispersed in such a saturated solution using sodium oleate in water as the emulsifying agent. Prismatic colors are secured.

Resorcinol also gives water high optical dispersive power. A saturated solution is readily dispersed in a Nujol solution of rubber, developing good color.

For a beautiful lecture demonstration one may shake together 4 volumes of glycerol and 4 volumes of a 2 to 4% solution of cellulose nitrate in amyl acetate. To this 5 to 10 volumes of benzene are added, then more glycerol until rather viscous and finally more benzene in small additions, with shaking, until colors appear. The final emulsion may contain over 30% of glycerol. To view it best a 125cc. oil specimen bottle is used as container and held some distance from the source of light. A single source is best. The colors are exhibited in a cell with parallel sides but not quite so beautifully as in the bottle. On standing, these emulsions "cream" downwards but vigorous shaking restores much of their beauty. In many cases this cream becomes an emulsion gel due, probably, to a flattening of the drops of glycerol as they exceed 74% volume of the cream and to a coagulation of the cellulose nitrate in interfacial films.

If a sheet of white paper be held close to the emulsion but between it and the source of light the colors disappear only to reappear if a narrow slit be cut in the paper. The ordinary spectroscope with fairly wide slit does not produce a pure spectrum. That is, all the colors overlap somewhat. If they overlap still more, white light is produced in the center.

If we used only monochromatic light, there could be no optical dispersion.

### Summary.

Two immiscible liquids can be emulsified, with suitable emulsifying agents such as cellulose nitrate, to produce (1) a transparent emulsion when (a) the refractive index of the two phases is the same, and (b) the dispersive power ( $n_F - n_C$ ) of the two phases is the same; (2) a chromatic (structural color) emulsion when (a) the refractive index of both phases is the same, and (b) the dispersive power of one phase is much greater than that of the other. The greater this difference the more intense the resulting color.

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**THE RELATION BETWEEN STATISTICAL MECHANICS AND THERMODYNAMICS.**

BY RICHARD C. TOLMAN.

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**I. Introduction.**

There have been two main methods of investigating the relation between statistical mechanics and thermodynamics, that of Gibbs and that of Boltzmann.

The method adopted by Gibbs was to study the properties of an ensemble of systems, each individual system of the ensemble being identical in structure with the actual physical-chemical system of interest. The systems of the ensemble were distributed in phase in accordance with the so-called canonical distribution law, and Gibbs was able to show that such a distribution is permanent and that the statistical-mechanical quantities determining this distribution have the properties of the thermodynamic quantities, free energy, energy, and temperature and was thus able to show in a very general and beautiful manner that the laws of thermodynamics are a natural consequence of statistical mechanics.

The method adopted by Boltzmann has been to consider a single physical-chemical system and study the distribution in phase of the molecules of this system when it has reached its configuration of maximum probability and hence of thermodynamic equilibrium. The law determining the distribution of the molecules in this state of equilibrium is known as the Maxwell-Boltzmann distribution law and although similar in form to the Gibbs canonical distribution law is not identical in content, since it deals with the distribution of molecules in a system instead of with the distribution of systems in an ensemble of systems. As to the relation between statistical mechanics and thermodynamics, Boltzmann has been able to show a fundamental connection between the probability of the configuration of the system at equilibrium and the entropy of the system and thus again to show that the laws of thermodynamics are a natural consequence of statistical mechanics.

The method of Boltzmann is perhaps somewhat less general than that of Gibbs, but leads perhaps more directly to very important information concerning the behavior of the individual molecules of the system. It is the method which will be adopted in this article.

Since Boltzmann, important investigations of the relation between the statistical mechanical quantity, probability, and the thermodynamic quantity, entropy, have been made by Planck. The work presented here will differ from that of Planck in two ways. In the first place, for the purpose of this article, we shall take no position with reference to the

quantum theory although the results obtained can easily be modified in accordance with the Planck quantum theory by assigning, as he does, a definite location and finite size  $G$  to the regions into which we divide the generalized space used in representing the phase of the individual molecules.<sup>1</sup> A more important difference between the method adopted in this article and that of Planck, is that instead of somewhat arbitrarily defining entropy, as a constant times the logarithm of probability, we shall endeavor to discover a statistical mechanical quantity which has the same derivatives with respect to the fundamental variables, energy  $E$ , volume  $v$ , and number of molecules  $N$ , as does entropy. This leads us to a somewhat different expression for entropy from that used by Planck, since the Planck expression although depending on the energy and volume in the correct manner does not make the entropy of a homogeneous system maintained at constant pressure and temperature vary proportionally to the number of molecules present. The Planck expression can be made to agree with ours by the addition of a term which is a function of the number of molecules present.<sup>2</sup>

<sup>1</sup> In another place (*Phys. Rev.*, 9, 261 (1918)) the writer has presented suggestions as to a method of reconciling quantum theory and statistical mechanics without giving up so much of the classical statistical mechanics as Planck has done.

<sup>2</sup> Many other investigators, besides Planck, have recently considered the relation between statistical mechanics and thermodynamics. Thus Marcelin, in his important contribution to the theory of physical chemical kinetics (*Ann. Phys.*, 3, 120 (1915)), has made use of a relation between free energy and a quantity occurring in the Maxwell-Boltzmann distribution law which the present writer believes to be incorrect. An article attempting to justify Marcelin's procedure has recently been published by E. P. Adams (*THIS JOURNAL*, 43, 1251 (1921)) but the present writer cannot agree with Adams' conclusions.

A comparison of equations obtained in this article with those obtained by Adams will show the lack of agreement. Expressing Maxwell's distribution law for a system of  $N$  molecules in the form

$$dN = e^{\frac{\psi - \epsilon}{kT}} dq_1 \dots dp_n$$

we shall obtain, in this article, for the Helmholtz free energy of the system, the expression

$$F = N\psi - N\bar{\epsilon} + E \quad (\text{Equation 35, this article})$$

while Adams obtains

$$F = N\psi. \quad (\text{Equation 10, } op. cit.)$$

The two equations become identical only for a perfect gas.

For the partial molal free energy of the substance involved, we shall obtain the expression

$$\left( \frac{\partial F}{\partial n} \right)_{\psi, T} = N_A \psi + RT. \quad (\text{Equation 39, this article})$$

where  $n$  is the number of mols and  $N_A$  is Avogadro's number, while Adams obtains

$$\partial F / \partial n = N_A \psi. \quad (\text{See Equation 11 and preceding discussion, } op. cit.)$$

The two equations are not even the same for the case of a perfect gas.

## II. Derivation of the Maxwell-Boltzmann Distribution Law.

In order to obtain the desired conclusion, it will be necessary to review in a fundamental way the derivation of the Maxwell-Boltzmann distribution law

$$dN = C e^{\frac{-\epsilon}{kT}} dq_1 \dots dp_n$$

where  $dN$  is the number of molecules having coördinates and momenta falling in the infinitesimal range  $dq_1 \dots dp_n$ . In particular we shall find it necessary to analyze with considerable care the meaning of the quantity  $\epsilon$  when it first enters the discussion. We shall find in general that  $\epsilon$  must be taken *not* as the energy of a molecule, having coördinates and momenta falling in a particular region  $dq_1 \dots dp_n$ , but *rather* as the rate of increase in the total energy of the system per molecule added to the region  $dq_1 \dots dp_n$  when the system is in its configuration of maximum probability. These two quantities are the same for dilute gases but for concentrated systems may be quite different. Hence the new methods which we introduce will be of considerable importance in dealing with the properties of imperfect gases or other concentrated systems.

1. **The System.**—For the purposes of this article we shall merely consider systems containing molecules or elements of a single kind. The methods employed, however, can easily be generalized to cover systems containing molecules, atoms, modes of vibration and so forth of any number of different kinds. We shall assume that the instantaneous state or phase of the system is determined by a specification of the generalized coördinates and momenta and that it obeys the laws of dynamics expressed for example in the Hamiltonian form.

2. **Probability of a Given Microscopic State.**—If  $Q_1 Q_2 \dots Q_m P_1 P_2 \dots P_m$  are generalized coördinates and momenta which can be used for describing the state of the system, we may think of the motion of the system as determined by the motion of a point in a  $2m$  dimensional space corresponding to the  $2m$  coördinates and momenta. We shall say that the *microscopic state* of the system at any instant is specified by a statement of the particular infinitesimal region of generalized space  $dQ_1 dQ_2 \dots dQ_m, dP_1 dP_2 \dots dP_m$  in which the representative point for the system in question is to be found. *We shall consider all the different possible microscopic states for a given system as equally probable.*

The justification for this assumption of equal probability for the different possible microscopic states has usually been based, in considerations of this kind, on the possibility of showing with the help of the Hamiltonian laws of motion, that an ensemble of similar systems with representative points uniformly distributed throughout the generalized space will permanently retain this uniform distribution. For our present purposes we shall accept this justification as sufficient and not attempt at this

time a more fundamental analysis of this feature of the classical statistical mechanics.

**3. Probability of a Given Statistical State.**—Let  $N$  be the number of elements (molecules) which go to make up the complete physical-chemical system in which we are interested. And let our imaginary division of the system into elements and our choice of coördinates be so made that the original  $2m$  generalized coördinates and momenta belonging to the whole system can be assigned to the individual elements of the system. Let  $q_1 q_2 \dots q_n p_1 p_2 \dots p_n$  be the coördinates and momenta belonging to a single element. We shall be specially interested then in the number of elements which have values of coördinates and momenta falling in any particular infinitesimal region

$$d\sigma = dq_1 dq_2 \dots dq_n dp_1 dp_2 \dots dp_n \quad (1)$$

We shall say that the statistical state of our system is specified by a statement of the number of elements of the various kinds which have values of their coördinates and momenta which fall in the different possible infinitesimal regions  $d\sigma$ .

It will be seen that the *microscopic state* of the system determines the coördinates and momenta for each individual element of the system, while the *statistical state* merely determines the number of elements of each of the different kinds which have coördinates and momenta falling in a particular range, without attempting to make any distinction as to which particular elements are taken to supply the quota.

We thus see that corresponding to a given statistical state there will be a large number of microscopic states which can be obtained by the inter-transposition of elements from one infinitesimal region to another without disturbing the total number in each region. Since we have already taken the microscopic states as equally probable, *we shall take the probability of any given statistical state as proportional to the number of microscopic states to which it corresponds.*

Let us specify a given statistical state by taking  $N_1 N_2 N_3 \dots$  as the number of elements having coördinates and momenta falling in the particular infinitesimal regions  $d\sigma_1, d\sigma_2, d\sigma_3$ , etc.

Then it is evident from the principles of permutation that the number of microscopic states corresponding to the given statistical state will be

$$W = \frac{N!}{N_1! N_2! N_3! \dots} \quad (2)$$

We shall call  $W$  the probability of the statistical state in question without introducing any proportionality factor.

Let us assume that each of the numbers  $N, N_1, N_2, N_3$ , etc., occurring in Equation 2 is large enough so that we may apply the Stirling formula for factorial  $N$

$$\underline{N} = \sqrt{2\pi N} \left(\frac{N}{e}\right)^N \quad (3)$$

Substituting in Equation 2, taking the logarithm of  $W$  and omitting negligible terms we obtain

$$\log W = N \log N - N_1 \log N_1 - N_2 \log N_2 \dots \quad (4)$$

which can be rewritten in the form

$$\log W = N \log N - \sum N_i \log N_i \quad (5)$$

where the summation  $\sum$  is to be taken over all the infinitesimal regions  $i=1,2,3,\dots$

**4. Statistical State of Maximum Probability.**—We shall be particularly interested in the statistical state of maximum probability which our system can assume with a *given number of molecules*, a *given energy content* and a *given volume*. Our interest in this state of maximum probability is due to the fact that we shall consider the system to be substantially in its state of maximum probability when thermodynamic equilibrium is attained.

Considering Equation 5, it is evident that the condition of maximum probability will be

$$\delta \log W = \delta \{ N \log N - \sum N_i \log N_i \} = 0 \quad (6)$$

This variation is not to be carried out entirely arbitrarily, however, since as stated above we shall not allow the number of molecules, the energy content nor the volume of the system to change.

Since the number of molecules is not to change we shall have

$$\delta N = \sum \delta N_i = 0 \quad (7)$$

As to the energy of the system  $E$ , it is evident that this is a function of the number of molecules  $N_1, N_2, N_3, \dots$  in each of the infinitesimal regions, and since this is to be constant we may write

$$\delta E = \sum \frac{\partial E}{\partial N_i} \delta N_i = 0 \quad (8)$$

As to the constancy of volume this is a matter of great importance since three of the coördinates  $q_1, \dots, q_n$  must necessarily correspond to the location of the infinitesimal region  $d\sigma$  in ordinary three-dimensional space, and hence if the volume of the container were varied this would lead to a variation in the total volume of the generalized  $2n$ -dimensional space  $\sigma$  and hence in the number of infinitesimal regions  $d\sigma_1, d\sigma_2, d\sigma_3$ , etc. Under the present circumstances we shall not be bothered with this possibility.

The simultaneous Equations 6, 7 and 8 may now be combined by the method of undetermined multipliers, giving us,

$$\sum \{ (\log N_i + 1) \delta N_i + \lambda \delta N_i + \mu \frac{\partial E}{\partial N_i} \delta N_i \} = 0$$

or

$$\sum \{ \log N_i + 1 + \lambda + \mu \frac{\partial E}{\partial N_i} \} \delta N_i = 0 \quad (9)$$



where the quantities  $\lambda$  and  $\mu$  are undetermined multipliers. Since the introduction of these multipliers makes the variations  $\delta N_i$  entirely arbitrary, it is evident that Equation 9 can only be true if the individual equations

$$\log N_i + 1 + \lambda + \mu \frac{\partial E}{\partial N_i} = 0 \quad (10)$$

are also true.

These equations can be put in a more convenient and familiar form if we introduce some different symbols. Let us put

$$\partial E / \partial N_i = \epsilon_i \quad (11)$$

$$\mu = 1/\theta \quad (12)$$

$$1 + \lambda = -\Psi/\theta \quad (13)$$

where the new symbols are defined by the equations given.

Substituting in (10) and solving for  $N_i$  we obtain

$$N_i = e^{\frac{\Psi - \epsilon_i}{\theta}} \quad (14)$$

This is an expression for the number of molecules whose coördinates and momenta fall in the  $i$ 'th infinitesimal region  $d\sigma$ , when the distribution is that of maximum probability, and hence is an expression of the Maxwell-Boltzmann distribution law.

**5. Introduction of a Continuous Variable.**—For purposes of mathematical convenience, in order to be able to use the language of integral calculus instead of that of summations, it is sometimes desirable to change Equation 14 by the introduction of continuous variables. If we do this, we may rewrite Maxwell's distribution law in the form<sup>3</sup>

<sup>3</sup> The symbols used in this formula were purposely chosen to agree with those used by Adams (THIS JOURNAL, 43, 1251 (1921)). The choice, however, may be somewhat misleading since the symbolism does not agree with the earlier use of Gibbs.

In Gibbs' use, the quantity  $e^{\frac{\Psi - \epsilon}{\theta}} dQ_1 \dots dP_m$  is the *fraction* of the total number of systems in a canonical ensemble of systems having coördinates and momenta falling in a particular infinitesimal range, and it can be shown that  $\psi$  may be taken as the Helmholtz free energy of a single system chosen from the ensemble, the average value  $\bar{\epsilon}$  may be taken as sensibly equal to the energy of a single system and  $\theta$  may be put proportional to the absolute temperature.

In the use adopted in this article,  $e^{\frac{\Psi - \epsilon}{\theta}} d\sigma$  is the *number* of molecules having coördinates and momenta falling in a particular infinitesimal range,  $\psi$  is related to the Helmholtz free energy by Equation 39,

$$N_A \psi = \left( \frac{\partial F}{\partial n} \right)_{\sigma, T} - RT$$

the average value  $\bar{\epsilon}$  is related to thermodynamic quantities by Equation 40,

$$n N_A \bar{\epsilon} = E - F + n \left( \frac{\partial F}{\partial n} \right)_{\sigma, T} - nRT$$

and  $\theta$  is again proportional to the absolute temperature.

of molecules of the gas. As the proof is simple and well known<sup>4</sup> but somewhat long, it does not seem desirable to repeat it here, since we are more particularly interested in the thermodynamic significance of  $\psi$  and  $\epsilon$  concerning which there has been some doubt.

**3. The Expression for Entropy.**—In order to show the thermodynamic significance of  $\psi$  and  $\epsilon$  we shall obtain an expression for the entropy of the system which is dependent on these quantities.

Except for an additive constant, in which we are not now interested, the entropy of a *homogeneous* system can be completely defined by the thermodynamic equations

$$\left(\frac{\partial S}{\partial E}\right)_{\nu, N} = \frac{1}{T} \quad (20)$$

$$\left(\frac{\partial S}{\partial V}\right)_{E, N} = \frac{p}{T} \quad (21)$$

$$\left(\frac{\partial S}{\partial N}\right)_{p, T} = \frac{S}{N} \quad (22)$$

The first two of these equations are direct consequences of the fundamental equation

$$dS = \frac{dE + pdv}{T}$$

and the third equation results from the fact that the entropy of a system is always taken as the sum of the entropies of its parts, and hence for a *homogeneous* system, which has the same pressure and temperature throughout, the entropy of any part will be proportional to the number of molecules in the part taken.

The problem, now before us, is to find a statistical mechanical quantity which has the differential coefficients given by Equations 20, 21 and 22. We shall find that a solution of this problem is given by the equation

$$S = k \left( \frac{N\epsilon - N\psi}{\theta} \right)_{\text{av.}} \quad (23)$$

Substituting Equation 19, denoting the average value of  $\epsilon$  by the symbol  $\bar{\epsilon}$ , and noting in accordance with our previous discussion that since  $\psi$  is independent of  $\sigma$ , it and its average value are the same, we may rewrite the above in the form

$$S = \frac{N\bar{\epsilon} - N\psi}{T} \quad (24)$$

Let us now show that the quantity given by Equation (24) actually does obey Equations 20, 21 and 22. To do this we must first obtain a mathematical identity which we shall need in the discussion.

<sup>4</sup> See for example, Tolman, *Phil. Mag.*, 28, 583 (1914) or "The Theory of the Relativity of Motion," Chapter VIII, "The Chaotic Motion of a System of Particles," University of California Press, 1917.

In accordance with Maxwell's distribution law we may write

$$N = \int e^{\frac{\psi - \epsilon}{kT}} d\sigma$$

Differentiating with respect to the parameter  $E$ , keeping the other two parameters  $v$ , and  $N$  constant,<sup>6</sup> we obtain

$$0 = \left( \frac{\partial N}{\partial E} \right)_{v,N} = \int \frac{\partial}{\partial E} \left( e^{\frac{\psi - \epsilon}{kT}} \right) d\sigma = \int e^{\frac{\psi - \epsilon}{kT}} \frac{\partial}{\partial E} \left( \frac{\psi - \epsilon}{kT} \right) d\sigma \quad (25)$$

We may now determine the derivative of  $\frac{N\bar{\epsilon} - N\psi}{T}$  with respect to energy. Noting Equation 17 for the average value of a quantity, we may write.

$$\begin{aligned} \left( \frac{\partial}{\partial E} \frac{N\bar{\epsilon} - N\psi}{T} \right)_{v,N} &= \frac{\partial}{\partial E} \int e^{\frac{\psi - \epsilon}{kT}} \frac{\epsilon - \psi}{T} d\sigma \\ &= \int \frac{\partial}{\partial E} \left( e^{\frac{\psi - \epsilon}{kT}} \right) \frac{\epsilon - \psi}{T} d\sigma + \int e^{\frac{\psi - \epsilon}{kT}} \frac{\partial}{\partial E} \left( \frac{\epsilon - \psi}{T} \right) d\sigma \end{aligned}$$

Remembering that  $\psi$  and  $T$  are independent of  $\sigma$ , this may be rewritten in the form

$$\begin{aligned} \left( \frac{\partial}{\partial E} \frac{N\bar{\epsilon} - N\psi}{T} \right)_{v,N} &= \frac{1}{T} \int \frac{\partial}{\partial E} \left( e^{\frac{\psi - \epsilon}{kT}} \right) \epsilon d\sigma - \frac{\psi}{T} \int \frac{\partial}{\partial E} \left( e^{\frac{\psi - \epsilon}{kT}} \right) d\sigma + \int e^{\frac{\psi - \epsilon}{kT}} \frac{\partial}{\partial E} \left( \frac{\epsilon - \psi}{T} \right) d\sigma. \end{aligned}$$

In accordance with Equation 25, it is evident, however, that the last two terms in this equation are zero. As to the first term on the right hand side of the above equation, it is evident that the quantity  $\frac{\partial}{\partial E} \left( e^{\frac{\psi - \epsilon}{kT}} \right)$  is

the rate of change in the number of molecules in region  $d\sigma$  with change in  $E$ , while  $\epsilon$  is the rate in change of the energy per molecule added to the region  $d\sigma$ . Hence the value of the definite integral is evidently  $\partial E / \partial E = 1$ . Our expression thus reduces to

$$\left( \frac{\partial}{\partial E} \frac{N\bar{\epsilon} - N\psi}{T} \right)_{v,N} = \frac{1}{T} \quad (26)$$

thus agreeing with the first of the three necessary equations (20), (21) and (22).

Let us now proceed to show that the rate of change of  $\frac{N\bar{\epsilon} - N\psi}{T}$  with respect to volume has the required value.

<sup>6</sup> It should be noted that the constancy of  $v$  makes it possible to differentiate solely back of the integral sign, since under these circumstances the limits of integration are constant.

In our previous discussions we have made use of the principle that an isolated system, with a definite energy content  $E$  in a container of definite volume  $v$ , will assume the statistical state of maximum probability. For our present purposes, we shall make use of the equally valid principle, that the system will assume the statistical state of maximum probability when it is enclosed in a cylinder with walls which do not permit the transfer of energy and provided with a movable piston, thus allowing a simultaneous variation in the parameters  $E$  and  $v$ , in accordance with the equation

$$\delta E = -p \delta v. \quad (27)$$

Now we have already found, in accordance with Equation 18, that when the parameters  $E$  and  $v$  are not allowed to vary, the probability  $W$  of the state finally attained is given by the expression

$$\log W = \left( \frac{N\bar{\epsilon} - N\psi}{kT} \right) + N \log N - N \log d\sigma. \quad (28)$$

The variation in this quantity with the parameters  $E$  and  $v$  will evidently be

$$\delta \log W = \left( \frac{\partial}{\partial E} \frac{N\bar{\epsilon} - N\psi}{kT} \right)_{v, N} \delta E + \left( \frac{\partial}{\partial v} \frac{N\bar{\epsilon} - N\psi}{kT} \right)_{E, N} \delta v$$

In the special case that we are considering,  $W$  has the maximum possible value not only for changes in internal arrangement with constant values of  $E$  and  $v$  but also for variations in  $E$  and  $v$  which do not conflict with the restriction imposed by Equation 27. Hence by introducing Equation 27 and applying the condition for maximum probability, we obtain

$$-\left( \frac{\partial}{\partial E} \frac{N\bar{\epsilon} - N\psi}{kT} \right)_{v, N} p \delta v + \left( \frac{\partial}{\partial v} \frac{N\bar{\epsilon} - N\psi}{kT} \right)_{E, N} \delta v = 0$$

Multiplying by  $k$ , dividing by  $\delta v$ , and introducing the expression we have already found for the rate of change of  $\frac{N\bar{\epsilon} - N\psi}{T}$  with  $E$ , we obtain and

$$\left( \frac{\partial}{\partial v} \frac{N\bar{\epsilon} - N\psi}{T} \right)_{E, N} = \frac{p}{T} \quad (29)$$

have thus shown the desired agreement with the second of our three necessary equations (20), (21) and (22).

In order to show the agreement of the quantity that we have chosen for entropy with the third of the three equations, we shall first need to obtain an auxiliary equation by differentiating the expression for Maxwell's distribution law

$$N = \int e^{\frac{\psi - \epsilon}{kT}} d\sigma$$

with respect to the number of molecules  $N$ , holding the pressure  $p$  and temperature  $T$  constant. In carrying out such a differentiation, it is to

be noted that we cannot consider the limits of the definite integral as constant, since the volume  $v$  of a homogeneous system at a given pressure and temperature is evidently proportional to the number of molecules  $N$ , and the volume over which the generalized space  $d\sigma$  is to be integrated is proportional to  $v$ . Keeping this consideration in mind, we may write

$$\left(\frac{\partial N}{\partial N}\right)_{p, T} = \int \frac{\partial}{\partial N} \left( e^{\frac{\psi - \epsilon}{kT}} \right) d\sigma + \left( e^{\frac{\psi - \epsilon}{kT}} \right)_{\text{lim}} \frac{\partial \sigma_{\text{lim}}}{\partial N}.$$

Noting further that the last term in this equation is evidently itself equal to  $\partial N / \partial N$ , and that  $\partial \bar{\epsilon} / \partial N$  is obviously zero since we have in no way changed the condition inside of any given region  $d\sigma$ , we obtain

$$0 = \int e^{\frac{\psi - \epsilon}{kT}} \frac{1}{kT} \frac{\partial \psi}{\partial N} d\sigma$$

or remembering that  $\psi$  and its average value for the system are the same, we may write

$$\left(\frac{\partial \psi}{\partial N}\right)_{p, T} = 0 \quad (30)$$

We may now differentiate our expression for entropy with respect to  $N$ . We obtain

$$\left(\frac{\partial}{\partial N} \frac{N\bar{\epsilon} - N\psi}{T}\right)_{p, T} = \frac{\bar{\epsilon} - \psi}{T} + \frac{N}{T} \frac{\partial \bar{\epsilon}}{\partial N} - \frac{N}{T} \frac{\partial \psi}{\partial N}.$$

We have just shown, however, that the last term in this equation is equal to zero, and it is evident, moreover, that  $\partial \bar{\epsilon} / \partial N$  is zero, since with constant pressure and temperature the value of  $\epsilon$  for every region  $d\sigma$  remains unchanged. Hence we may rewrite the above equation in the form

$$\left(\frac{\partial}{\partial N} \frac{N\bar{\epsilon} - N\psi}{T}\right)_{p, T} = \frac{1}{N} \left(\frac{N\bar{\epsilon} - N\psi}{T}\right). \quad (31)$$

We have thus shown the agreement of the expression which we have chosen for entropy with the third and last of the three necessary equations (20), (21) and (22), and may now write

$$S = \frac{N\bar{\epsilon} - N\psi}{T}$$

or if desired

$$S = \frac{N\bar{\epsilon} - N\psi}{T} + N \times \text{const.} \quad (32)$$

**4. Other Equations Connecting Statistical Mechanics and Thermodynamics.**—Equation 32 shows perhaps as well as any, the thermodynamic significance of the statistical mechanical quantities  $\epsilon$  and  $\psi$ . A number of other equations interrelating the two methods of attack, however, will also be of interest.

Differentiating the expression for Maxwell's distribution law at constant volume and temperature we obtain

$$\begin{aligned}
 \left(\frac{\partial N}{\partial N}\right)_{s,T} &= 1 = \int \frac{\partial}{\partial N} \left( e^{\frac{\psi-\epsilon}{kT}} \right) d\sigma \\
 &= \int e^{\frac{\psi-\epsilon}{kT}} \frac{1}{kT} \frac{\partial \psi}{\partial N} d\sigma - \int e^{\frac{\psi-\epsilon}{kT}} \frac{1}{kT} \frac{\partial \epsilon}{\partial N} d\sigma \\
 \text{or } kT &= \int e^{\frac{\psi-\epsilon}{kT}} \frac{\partial \psi}{\partial N} d\sigma - \frac{\partial}{\partial N} \int e^{\frac{\psi-\epsilon}{kT}} \epsilon d\sigma + \int \frac{\partial}{\partial N} \left( e^{\frac{\psi-\epsilon}{kT}} \right) \epsilon d\sigma
 \end{aligned}$$

An inspection of the last term of this equation shows that it is equal to  $\partial E/\partial N$ . Introducing Equation 17 for the average value of a quantity, remembering the relation between  $\psi$  and its average value, and solving for  $\partial E/\partial N$ , we obtain,

$$\left(\frac{\partial E}{\partial N}\right)_{s,T} = \bar{\epsilon} + N \left(\frac{\partial \bar{\epsilon}}{\partial N}\right)_{s,T} - N \left(\frac{\partial \psi}{\partial N}\right)_{s,T} + kT. \quad (33)$$

This is an equation of some interest, owing to the thermodynamic importance of the quantity  $\partial E/\partial N$ .

Another thermodynamic quantity of importance is the Helmholtz free energy which may be defined by the equation

$$F = E - TS. \quad (34)$$

Introducing the expression for entropy given by Equation 32, we have,

$$F = N\psi - N\bar{\epsilon} + E. \quad (35)$$

an equation which reduces to

$$F = N\psi \quad (36)$$

for the special case of a perfect gas.

The derivative of  $F$  with respect to  $N$ , at constant volume and temperature is also of interest. We have

$$\left(\frac{\partial F}{\partial N}\right)_{s,T} = \psi + N \left(\frac{\partial \psi}{\partial N}\right)_{s,T} - \bar{\epsilon} - N \left(\frac{\partial \bar{\epsilon}}{\partial N}\right)_{s,T} + \left(\frac{\partial E}{\partial N}\right)_{s,T}$$

which, on substitution of Equation 33, becomes

$$\left(\frac{\partial F}{\partial N}\right)_{s,T} = \psi + kT \quad (37)$$

or putting

$$N = n N_A \quad (38)$$

where  $n$  is the number of mols in the system and  $N_A$  is Avogadro's number, Equation 37 becomes

$$\left(\frac{\partial F}{\partial n}\right)_{s,T} = N_A \psi + kT \quad (39)$$

or

$$N_A \psi = \left(\frac{\partial E}{\partial n}\right)_{s,T} - kT.$$

This equation shows in a very simple way the thermodynamic significance of  $\psi$ , since except for  $\psi$  it contains none but thermodynamic quantities.

A similar equation containing  $\epsilon$  and none but thermodynamic quantities is, of course, impossible since it is the average value of  $\epsilon$  rather than its value for any particular region  $d\sigma$  that has thermodynamic significance. An equation containing the average value  $\bar{\epsilon}$  and none but thermodynamic quantities can be obtained by substituting (38) and (39) in our expression for entropy Equation 32, we obtain

$$n N_A \bar{\epsilon} = E - F + n \left( \frac{\partial F}{\partial n} \right)_{v,T} - nkT \quad (40)$$

which can be shown to reduce to

$$n N_A \bar{\epsilon} = E \quad (41)$$

for the special case of a perfect gas.

#### IV. Comparison with Results of Planck.

In conclusion it will be of interest to compare the expression which we have obtained for the entropy of a system with that of Planck.\*

Planck defines entropy by the equation

$$S = k \log W \quad (42)$$

where  $W$  is the probability of the configuration. We, on the other hand, have taken the quantity

$$S = \frac{N\bar{\epsilon} - N\psi}{T} \quad (43)$$

as entropy, since it has the same derivatives with respect to energy, volume, and number of molecules as does entropy.

In order to compare our equation with that of Planck, we may introduce into (43) the expression which we obtained for probability, as given by Equation 18. We obtain

$$S = k \log W - kN \log N + kN \log d\sigma. \quad (44)$$

It is apparent that our expression for entropy and that of Planck differ from each other in an important manner, and that this difference is not merely due to the fact that in accordance with the classical statistical mechanics we have divided our generalized space  $\sigma$  into infinitesimal regions of equal size  $d\sigma$ , while Planck in accordance with his form of quantum theory divides the space  $\sigma$  into regions of finite size  $G$ .

Both our expression for entropy and Planck's have the same derivatives with respect to energy and volume, but different derivatives with respect to the number of molecules  $N$ . This is a fundamental difference between the expressions and the reason why Planck's expression for entropy is not satisfactory when considerations are to be undertaken which involve a change in the number of elements.

\* The difficulties involved in defining entropy by the equation  $S = k \log W$  and at the same time making the entropy of a system equal to the sum of the entropies of its parts have also been pointed out by Mrs. T. Ehrenfest-Afanassjewa, *Verslag. Akad. Wetenschappen Amsterdam*, 21, 53 (1919).

In order to make this point entirely clear, let us take Planck's expression for entropy using finite regions and summations as he does.

The Planck expression for entropy may be written

$$S = k \log W = kN \log N - k \sum N_i \log N_i \quad (45)$$

$$i = 1, 2, 3, \dots, m$$

where the summation is to be carried out over all the regions  $i = 1, 2, 3, \dots, m$  that contain molecules.

Consider the change in this quantity corresponding to a change  $\delta N$  in the number of molecules, pressure and temperature being maintained constant. For a *homogeneous* system it is evident that the number of molecules falling in any particular region will not be changed provided temperature and pressure are maintained constant. Hence we may write

$$(\delta S)_{p,T} = k (\log N + 1) \delta N - k \sum_{i=(m+1) \dots (m+\delta m)} N_i \log N_i \quad (46)$$

where the summation is carried out over the new regions  $(m+1) (m+2) \dots (m+\delta m)$  which have been created by the increase in volume which accompanies the increase in number of molecules.

Owing to the similarity of the distribution in the new regions to that in the old, it is evident that we may rewrite the last term in the form

$$\sum_{i=(m+1) \dots (m+\delta m)} N_i \log N_i = \left\{ \sum_{i=1,2,3,\dots,m} N_i \log N_i \right\} \frac{\delta N}{N} \quad (47)$$

Substituting (6) and dividing by  $\delta N$  we obtain

$$\left( \frac{\delta S}{\delta N} \right)_{p,T} = k \log N - \frac{k}{N} \sum N_i \log N_i + k. \quad (48)$$

We note that  $\left( \frac{\delta S}{\delta N} \right)_{p,T}$  is not equal to  $S/N$  as is required for a successful definition of entropy.

For a successful definition along the Planck lines we might suggest

$$S = k \log W - kN \log N. \quad (49)$$

This expression would make the entropy of a system at constant pressure and temperature proportional as it should be to the total number of molecules present. It would also make the absolute numerical value of  $S$  depend on the finite size  $G$ , which Planck chooses for his regions of equal probability, in the way that Planck desires. It should further be pointed out that there is no disagreement between Equation 49 and our own Expression 44 since we have already called attention to the fact (see Equation 32) that it is allowable to add to our expression for entropy any desired constant multiplied by  $N$ .

### Summary.

1. The relation between statistical mechanics and thermodynamics has been investigated in this article by a method which is based like that



of Boltzmann and Planck on a consideration of the arrangement of the elements or molecules of a system. Instead, however, of following the procedure of Boltzmann and Planck by somewhat arbitrarily defining entropy by the equation

$$S = k \log W$$

the attempt has been made in this article to discover a statistical mechanical quantity which has the same derivatives with respect to energy, volume and number of molecules as does the thermodynamic quantity entropy. In this way we have been led to an expression for entropy which differs from that of Planck by an additive term, and have shown that the addition of such a term is, as a matter of fact, necessary in order that the derivative of the entropy of the system with respect to number of molecules shall have its correct value.

2. In connection with the derivation, it has been shown that the quantity  $E$  occurring in the Maxwell-Boltzmann distribution law

$$dN = C e^{-\frac{E}{kT}} dq_1 \dots dp_n$$

must be taken, *not* as the energy of a molecule having coördinates and momenta falling in the region  $dq_1 \dots dp_n$ , but *rather* as the rate of increase in the total energy of the system per molecule added to the region  $dq_1 \dots dp_n$ , when the system is in its configuration of maximum probability. These two quantities are the same for dilute gases, but for concentrated systems may be quite different. Hence the new methods which are introduced may be of considerable importance in dealing with the properties of imperfect gases or rather concentrated systems.

3. It was pointed out that the equations obtained in this article connecting the statistical mechanical quantities occurring in the Maxwell-Boltzmann distribution law with thermodynamic quantities, do not agree with the equations of Marcelin and Adams.<sup>2</sup>

WASHINGTON, D. C.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA.]  
**THE DISTRIBUTION OF THERMAL ENERGY IN THE TETRACHLORIDES OF CARBON, SILICON, TITANIUM AND TIN.**

By WENDELL M. LATIMER.

Received October 20, 1921.

The determination of the specific heats and heats of fusion of several tetrachlorides of the fourth periodic group was undertaken in connection with the study of the effect of mass upon the distribution of thermal energy. When the conditions in a solid are such that the thermal energy is distributed according to the principle of the equipartition of energy, the specific heat per gram atom is independent of the mass; however, when the "equipartition conditions" are not fulfilled, whatever the exact nature of

the cause may be, the deviation of the specific heat from the value of  $3R$  is larger the smaller the mass of the atoms and the greater the constraints or forces under which the atoms are vibrating.<sup>1</sup> In any one case, it has been impossible to state just how much the specific heat is affected by each of these two factors, especially since the actual forces between the atoms are not known quantitatively, but are estimated in terms of compressibility, atomic volume melting points, hardness, etc.

The tetrachlorides, however, seem to offer an unusual opportunity for studying the effect due to the mass, since there is considerable evidence that in these compounds the constraints are quite similar. In the first place, at room temperature they are similar non-polar liquids, and it seems quite likely that this non-polar nature is preserved in the solid state. Then if each positive atom is surrounded by 4 chlorine atoms, the solid would be held together by forces acting largely between the chlorine atoms of adjacent molecules, and the constraints in the solid would be not only small but practically the same for all these compounds. This type of solid in which the molecule preserves its identity is quite different from the polar solids such as the alkali halides. Here the molecule has lost its identity, that is, it is impossible to say that a given positive atom belongs to any one negative atom, and the solid is held together by forces which are larger the greater the difference in the positive and negative nature of the elements.

These conclusions, which might be drawn from the molecular structure, as to the similarity of the constraints in the tetrachlorides, are confirmed by consideration of the melting-point data, Table I.

TABLE I  
MELTING-POINT DATA

	M. p. °C.		M. p. °C.		M. p. °C.
CCl <sub>4</sub>	-24	NaH	high, decomposes	CH <sub>4</sub>	-186
SiCl <sub>4</sub>	-70	NaF	980	CF <sub>4</sub>	- 80
TiCl <sub>4</sub>	-30	NaCl	804	CCl <sub>4</sub>	- 24
SnCl <sub>4</sub>	-33	NaBr	757	CBr <sub>4</sub>	92
PbCl <sub>4</sub>	-15	NaI	653	Cl <sub>4</sub>	decomposes

The agreement in the melting points of the tetrachlorides, which is quite close, is made more striking by comparison with the melting points of the sodium halides, which not only are much higher but vary in the order of the increasing polarity of the compounds. On the other hand, the melting points of the tetra-halogen carbon compounds vary in the same order as the melting points of the halogens themselves, again indicating that these solids are held together by forces acting between halogen atoms of adjacent molecules. Indeed many additional cases, such as the almost exact agree-

<sup>1</sup> Einstein, *Ann. Physik*, [4] 34, 170 (1911). Lewis and Adams, *Phys. Rev.*, 4, 331 (1914).

ment of the melting points of methane and silicane, might be cited as indicating that in general the constraints in the non-polar tetra-compounds depend largely upon the nature of the four negative atoms, and are more or less independent of the positive atom.

### Experimental.

The specific heats of carbon, silicon, titanium and tin tetrachlorides were measured from the temperature of liquid air to 298° K, and, in addition, the specific heat of carbon tetrachloride was measured at still lower temperatures in order to determine the whole specific heat curve for these compounds. The heats of fusion and, in the case of carbon tetrachloride, a heat of transition, were also determined, thus giving the total thermal content at 298° K.

**Method.**—The method and experimental procedure employed in the measurements of specific heat between the temperatures of liquid air and 25° C were essentially the same as described in a previous paper.<sup>2</sup> In the determination of the heats of fusion the heating coil of the calorimeter was modified by decreasing the resistance in order that the rate of input of energy might be greatly increased. These values are probably accurate to within 2%.

**Liquid Hydrogen Cryostat.**—In order to obtain temperatures below 80° K, a small liquid hydrogen cryostat has been constructed. The details of construction will be given in a later paper. Advantage was taken of the Joule-Thomson effect of hydrogen precooled with liquid air. The success of the cryostat resulted from the use of a very efficient heat interchanger of small flattened and twisted copper tubing designed by Mr. George F. Nelson, mechanician of this laboratory. The coils of the interchanger surrounded the calorimeter and were insulated from the calorimeter and from the surrounding bath of liquid air by enclosing the coils in a brass case in which a high vacuum was maintained. Since radiation is small at these temperatures the only source of heat leaks was through the single connecting tube through which passed the coil for the incoming high-pressure hydrogen and the outgoing cold expanded hydrogen. The hydrogen was supplied by a battery of five cylinders at an initial pressure of 140 atmospheres.

**Measurement of Temperature.**—Between 60° and 300° K the copper-constantan couple calibrated by Eastman and Rodebush<sup>3</sup> was available. The values for the e. m. f. of this couple may probably be extrapolated to 40° K without making a large error. The temperature of the liquid hydrogen cryostat could not be accurately determined from the boiling point of hydrogen since the back pressure of the expanded hydrogen in the

<sup>2</sup> Gibson, Latimer and Parks, *THIS JOURNAL*, 42, 1533 (1920).

<sup>3</sup> Eastman and Rodebush, *THIS JOURNAL*, 40, 489 (1918).

coils was not known. The construction of the cryostat is such that a hydrogen or helium thermometer could not be used. Specific heat measurements at the lower temperatures were made in terms of a constantan resistance thermometer. It is hoped that investigations now under way will soon establish an accurate low temperature scale for this laboratory.

**Purification of Materials.**—Imported tetrachlorides of carbon, silicon and tin were used. The titanium tetrachloride was prepared from rutile. Each tetrachloride was distilled at a low pressure into a specially constructed U-tube which was then sealed.

The liquid was purified, first, by cooling almost to the freezing point and filtering out

TABLE II

## EXPERIMENTAL RESULTS

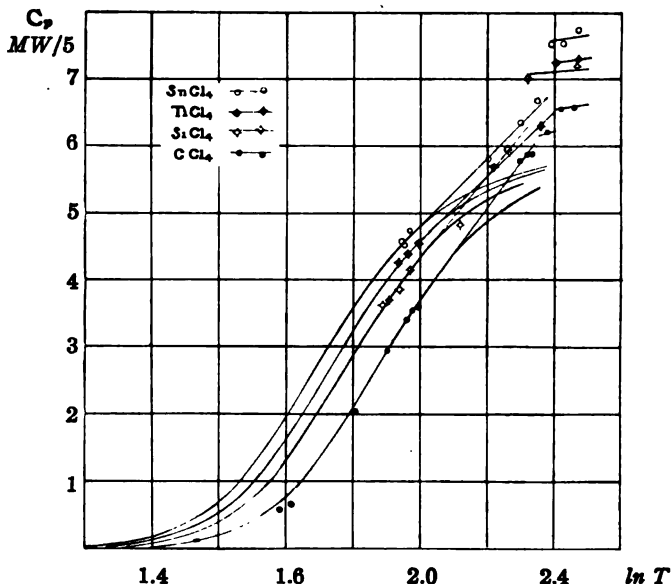
Carbon Tetrachloride			Silicon Tetrachloride			
	Temp. ° K	$C_p$ per MW/5		Temp. ° K	$C_p$ per MW/5	
Solid <sub>2</sub> .....	39.1	0.60	Solid.....	77.4	3.60	
	40.7	0.65		81.8	3.70	
	63.8	2.05		86.6	3.83	
	79.6	2.81		94.8	4.14	
	91.0	3.40		131.3	4.80	
	95.0	3.57		168.6	5.68	
	99.5	3.60		181.0	5.95	
	199.5	5.84		185.8	6.08	
	204.1	5.90		Liquid.....	208.8	6.74
	208.0	5.90			294.3	6.94
Solid <sub>1</sub> .....	229.4	6.20	Heat of fusion at 203.3° K, 10.85 cal. per gram.			
	232.5	6.29				
	235.6	6.22				
	238.0	6.77				
Liquid.....	253.8	6.40				
	265.1	6.30				
	290	6.34				
Heat of transition at 224.6° K, 7.10-7.19 cal. per gram.						
Heat of fusion at 249° K, 4.1-4.22 cal. per gram.						
Titanium Tetrachloride			Tin Tetrachloride			
	Temp. ° K	$C_p$ per MW/5		Temp. ° K	$C_p$ per MW/5	
Solid.....	86.7	4.26	Solid.....	89.0	4.59	
	92.8	4.40		89.5	4.53	
	99.3	4.54		95.0	4.73	
	194.6	6.19		95.9	4.71	
	231.8	6.31		161.2	5.89	
	247.7	6.21		200.5	6.32	
	251.6	7.26		200.7	6.33	
	294.3	7.32		205.0	6.26	
Liquid.....	251.6	7.26	Liquid.....	227.3	6.62	
	294.3	7.32		266.1	7.56	
Heat of fusion at 248.0° K, 11.77 cal. per gram.			Heat of fusion at 239.9° K, 8.38- 8.42 cal. per gram.			

any solid impurities which separated, and second, by repeated crystallization pouring off each time that portion of the liquid which remained after most of the sample had crystallized. Both of these operations could be carried out in the same sealed U-tube. The rise in the values of the specific heat just below the melting point was very marked when the unpurified compounds were used, but was decreased enormously by the purification carried out. The melting point of the purified silicon tetrachloride was approximately  $20^\circ$  higher than the value given in the literature.

The experimental results are summarized in Table II. Measurements on carbon tetrachloride at lower temperature have not been included because of the uncertainty in regard to the accuracy of the temperature scale.

### Discussion of Results.

In Fig. 1 the so-called "Class I" or Debye<sup>4</sup> curves have been drawn for  $C_p$  per average gram atom against  $\log T$ . These curves are all the same



function of  $T/\theta$ , where  $\theta$  is a constant which shifts their position along the  $\log T$  axis. Although the specific heat of most metals follows this regular curve, the specific heats of compounds in general do not, and a great many explanations have been offered for the deviations.<sup>5</sup> It seems to the writer that this curve probably represents the manner in which a single atom gains thermal energy, and only when all the atoms of a substance are of similar mass and held by similar constraints will the  $C_p$  curve for the substance be of the same form. Hence for a compound such as mercurous

<sup>4</sup> Lewis and Gibson, *THIS JOURNAL*, 39, 2534 (1917).

<sup>5</sup> Lewis, "A System of Physical Chemistry," Longmans, Green and Co., 1919, Vol. 3.

chloride, even though both the mercury and chlorine atoms gain thermal energy according to this typical curve, the  $C_p$  curve for the mercury will lie above that for the chlorine, and the  $C_p$  curve for the compound, which must be the average of the two, will deviate from this typical curve. On the other hand, the  $C_p$  curve for potassium chloride agrees very closely with the regular curve due to the close agreement of the masses of the potassium and chlorine atoms. Examples of the quantitative agreement of the average specific heat curves with the mean of two Class I curves could be given for many substances. In the case of the tetrachlorides the curves for silicon and titanium should follow the shape of the regular curve very closely. The greatest deviation is to be expected with tin tetrachloride, but since there are 4 chlorine atoms to 1 atom of tin, even in this case, the error introduced in assuming the regular curve for extrapolating over the low temperature should not be very great. The deviation of the  $C_p$  values at higher temperatures is due of course, to the increasing difference between  $C_p$  and  $C_v$ . From these curves the entropies of the 4 compounds have been calculated. These calculations are summarized in Table III.

TABLE III  
ENTROPIES OF FOUR TETRACHLORIDES

	CCl <sub>4</sub>	SiCl <sub>4</sub>	TiCl <sub>4</sub>	SnCl <sub>4</sub>
$S_{TP}$ Solid II.....	31.80	.....	.....	.....
$\Delta H$ of transition..1100	.....	.....	.....	.....
$T$ of transition. 224.6	.....	.....	.....	.....
$\Delta S$ of transition.....	4.90	.....	.....	.....
$S_{mp}$ Solid I.....	3.14	33.85	43.80	44.50
$\Delta H$ of fusion....644	.....	18.45	22.33	21.88
$T$ of fusion....249° K	.....	203.3	248°	23.99
$\Delta S$ of fusion.....	2.59	9.08	9.01	9.11
$S$ liquid.....	6.63	13.50	6.70	8.23
<hr/>				
$S_{298}$ .....	49.06	56.43	59.51	61.84
$\Delta S_{298}$ of formation....	-50.84	-48.27	-47.09	-49.66
$\Delta H_{298}$ of formation....	-75.700	-128.100	.....	-128.010
$\Delta F_{298}$ of formation....	-60.550	-113.710	.....	-113.210

The value  $S_{TP}$ , Solid II, for carbon tetrachloride, 31.80, is the entropy,  $\int_T \frac{C_p dT}{T}$ , of the crystalline form stable at low temperatures, at its transition point. Since  $C_p$  has been plotted against  $\log T$ , the entropy is given by the area under the curve. The increase of entropy by the transition  $\Delta H/T$  is 4.90; the increase of entropy of Solid I from the transition point to the melting point, obtained again from the area under the curve, is 2.14; the entropy of fusion, 2.59; and the gain of entropy of the liquid from the melting point to 298° K, 6.63. The sum of these values gives  $S_{298}$  for

liquid carbon tetrachloride, 49.06. In the row designated as  $\Delta S_{298}$  of formation, the figures given are the calculated values for the entropy of formation of the compounds from their elements. In calculating these values  $S_{298}$  of the elements chlorine, carbon, silicon, titanium and tin were taken as 25, 1.3, 2.7, 6.6, and 11.5, respectively. The heats of formation<sup>6</sup> of these compounds are also given in the table. Although these values are probably not of great accuracy, they have been used in calculating the free energy of formation of the compounds from their elements by the relation  $\Delta F = \Delta H - T \Delta S$ .

It will be observed that the entropies of the compounds increase, as is to be expected, in the order of increasing molecular weight. The most striking fact, however, is the close agreement of the entropies of formation; for although the entropies of the compounds differ by more than 13 entropy units, the entropies of formation differ by less than 4 units. In other words, the entropy of the compound is the sum of the entropies of the elements minus a constant. This indicates that the difference in the entropies of the tetrachlorides is due entirely to the difference in the mass of the positive atoms. Quantitatively this difference is approximately

$$3/2 R \ln \frac{\text{at. wt.}_1}{\text{at. wt.}_2}$$

This relation accounts very closely for the difference in entropy of all the solid compounds whose elements have a value for their Kopp's-law constant of approximately  $-3 R$ . Since the constraints in these compounds obviously vary within rather wide limits, it would seem the conclusion must be drawn that there is a limiting value for the constraints below which the effect upon the entropy is negligible. The data for a large number of compounds, including the tetrachlorides, have been discussed in a previous paper.<sup>7</sup>

Although a survey of the data on the entropy of fusion of a large number of substances shows certain marked relationships, it is impossible to make any generalization such as Trouton's rule for the entropy of vaporization. However, the agreement of the entropies of fusion of silicon, titanium and tin tetrachlorides indicates that such a relationship, although masked by other factors in many cases, does exist. The entropy of a substance is a measure of the complexity of thermal motion. Now while the complexity of thermal motion in many liquids is doubtless much the same, the complexity of motion of the atoms in a solid with low constraints must be quite different from that in a solid with high constraints. Hence, it is not surprising that the entropy of fusion varies far more than the entropy of vaporization, and yet is constant for many classes of solids. The

<sup>6</sup> Landolt-Börnstein, "Tabellen."

<sup>7</sup> Latimer, *THIS JOURNAL*, 43, 818 (1921).

entropy of fusion of chlorine, 9.5 entropy units, agrees well with the value found for the three tetrachlorides.

### Summary.

The specific heats of carbon, silicon, titanium and tin tetrachlorides have been measured from the temperature of liquid air to 298° K and, in addition, the specific heat of carbon tetrachloride was measured at still lower temperatures in order to determine the whole specific-heat curve for these compounds. The heats of fusion and, in the case of carbon tetrachloride, a heat of transition, were also determined, thus giving the total thermal content at 298° K.

The entropy of each of the compounds at 290° K and the entropy change in the formation of the compound from its elements have been calculated, and the results considered in reference to the mass of the atoms involved.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD COLLEGE.]

## INDUCTION PERIODS IN REACTIONS BETWEEN THIOSULFATE AND ARSENITE OR ARSENATE:<sup>1</sup> A USEFUL CLOCK REACTION.

BY GEORGE SHANNON FORBES, HOWARD WILMOT ESTILL, AND OSMAN JAMES WALKER.

Received October 26, 1921.

Vortmann<sup>2</sup> in 1889 obtained arsenious sulfide from arsenite or arsenate and thiosulfate in acid solution. Neither he nor any later worker in this field<sup>3</sup> mentions the reaction's sharp and highly reproducible induction period, though von Szilágyi says that the compound  $K_2As(S_2O_3)_3$ , which he obtained from arsenious chloride, potassium chloride and sodium thiosulfate "decomposes in water solution, in a shorter or longer time, according to concentration and temperature, and deposits  $As_2S_3$ ."

Molal arsenite solution was prepared from sodium hydroxide and purest commercial arsenious oxide. Each portion used was converted to arsenious acid by the calculated volume of standard hydrochloric acid. Molal thiosulfate solution was standardized against iodine, purified, re-sublimed and dried. Standard solutions of hydrochloric and acetic acids were referred ultimately to properly dehydrated sodium carbonate.

Into one beaker we discharged from burets arsenite, water, neutralizing acid, and acetic or hydrochloric acid in excess; into a larger beaker,

<sup>1</sup> The work on arsenates was performed mainly by O. J. Walker.

<sup>2</sup> Vortmann, *Ber.*, 22, 2308 (1889).

<sup>3</sup> Weinland and Gutmann, *Z. anorg. Chem.*, 17, 409 (1898).

Mackenzie and Marshall, *J. Chem. Soc.*, 93, 1726 (1908).

Gutmann, *Ber.*, 38, 1728, 3277 (1905); J. von Szilágyi, *Z. anorg. allgem. Chem.*, 40, 2818 (1907); 41, 1650 (1908).

113, 75 (1920).



water and thiosulfate. All the volumes were planned to give the desired concentrations in a total volume of 100 cc. The two solutions, brought to 22.0°, were quickly and thoroughly mixed, noting the time by an ordinary watch, or by a stop-watch held by a second person if the period was short. The precipitate suddenly appeared from a clear solution after an interval fixed by temperature and concentration, which was carefully recorded. Table I gives induction periods in seconds with acetic acid in excess. These are inversely proportional to thiosulfate concentration over a wide range. They are almost independent of the other concentrations.

TABLE I  
INDUCTION PERIODS WITH ACETIC ACID IN EXCESS  
Millimoles of Sodium Thiosulfate per Liter

<i>M</i> H <sub>2</sub> AsO <sub>3</sub> Mmoles.	HAc S <sub>2</sub> O <sub>3</sub> Mmoles.	800 Sec.	400 Sec.	320 Sec.	240 Sec.	200 Sec.	80 Sec.
20	4	..	24	..	..	48	127
20	2	..	25	..	..	50	130
80	4	..	25	32	42	..	130
80	2	13	25	33	45	..	120
• 80	1	..	27	32	47	..	145

This reaction is highly suitable for lecture demonstrations both of induction periods and of the simplest relation between concentration and reaction velocity. The familiar reaction liberating iodine from iodate and sulfurous acid is less satisfactory, as its ingredients are less stable, and the time-concentration relations highly complicated.<sup>4</sup> The normal temperature coefficient of the induction velocity suggests another good experiment.

Vortmann gives the reaction:  $2\text{H}_2\text{AsO}_3 + 9\text{H}_2\text{S}_2\text{O}_3 = \text{As}_2\text{S}_3 + 3\text{SO}_2 + 9\text{H}_2\text{O} + 3\text{H}_2\text{S}_4\text{O}_6$ , while von Szilágyi finds, in concentrated solution, that  $\text{AsCl}_3 + 3\text{KCl} + 3\text{Na}_2\text{S}_2\text{O}_3 = 6\text{NaCl} + \text{K}_3\text{As}(\text{S}_2\text{O}_3)_3 = 6\text{NaCl} + 3\text{K}_2\text{S}_2\text{O}_6 + \text{As}_2\text{S}_3$ . We have been unable to resolve either of the above reactions into stages which give the relations between time and reaction velocity observed by us. If the slowest stage is a unimolecular decomposition of thiosulfate, this must proceed in an unfamiliar fashion, as it is retarded by increasing hydrogen-ion concentration.

No analogy with the Landolt reaction, where the final product is for a time consumed by an original reactant, appears valid. This much, however, may be said,—the induction period is probably not a coagulation time effect, as it is not materially affected by excess of acetic acid, or by aluminum salts.

Table II shows that hydrogen ions beyond half the thiosulfate concentration greatly prolong the periods. Below this value, these are independent of acid concentration, hydrochloric or acetic. Arsenious sulfide,

<sup>4</sup> Eggert, *Z. Elektrochem.*, 23, 8 (1917).

then, forms less readily from thiosulfate decomposed by excess of hydrogen ion. Strangely enough, one mol of arsenite or arsenate will prevent 20 or more mols of thiosulfate from separating free sulfur when treated with large excess of hydrochloric acid.

The induction periods become somewhat longer if arsenate replaces arsenite. In general no sulfide appears unless there are over two mols

TABLE II  
EFFECT OF HYDROGEN ION ON INDUCTION PERIODS. TIME IN SECONDS  
 $\text{H}_2\text{AsO}_3$  constant at 80 millimoles per liter

$\text{Na}_2\text{S}_2\text{O}_3$ per liter Mmoles.	$\text{HCl}/\text{Na}_2\text{S}_2\text{O}_3$						$\text{HAc}/\text{Na}_2\text{S}_2\text{O}_3$		
	4	2	1	$1/2$	$1/4$	$1/8$	4	2	1
400	240	120	..	..	..	..	25	25	27
320	300	120	60	35	30	30	32	33	32
280	360	210	125	42	33	34	..	..	..
240	1260	780	150	50	40	40	42	45	47
80	3120	1500	..	..	..	..	130	120	145

of thiosulfate and of hydrogen for each mol of arsenic acid. Great excess of one reactant, especially of thiosulfate, compensates for deficiency in

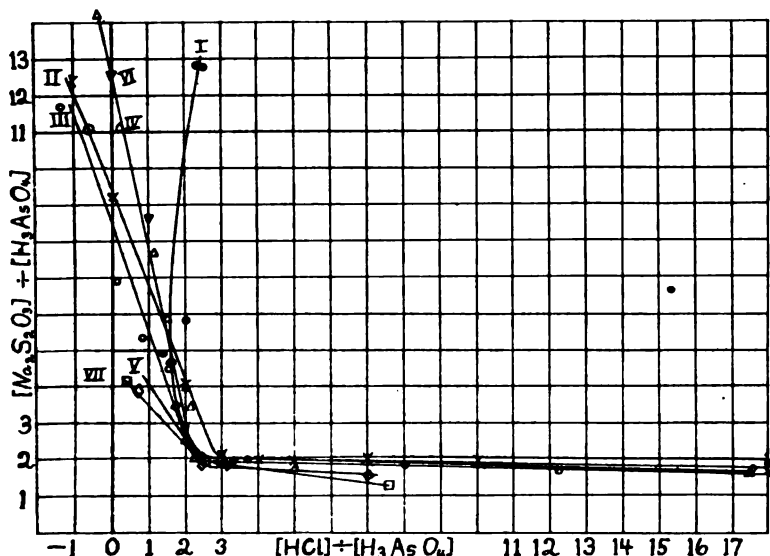


Fig. 1.

the other. Each curve in Fig. 1 represents a solution containing one constant concentration; in I, 0.06  $M$   $\text{Na}_2\text{S}_2\text{O}_3$ ; II, 0.05  $M$   $\text{H}_2\text{AsO}_4$ ; III, 0.07  $M$   $\text{H}_2\text{AsO}_4$ ; IV, 0.25  $M$   $\text{Na}_2\text{S}_2\text{O}_3$ ; V, 0.14  $M$   $\text{H}_2\text{AsO}_4$ ; VI, 0.02  $M$   $\text{H}_2\text{AsO}_4$ ; VII, 0.25  $M$   $\text{H}_2\text{AsO}_4$ . Each point, located by trial, gives a concentration ratio yielding the barest turbidity after a long time. The area below and to the left of each curve includes all ratios which yield no precipitate.

Mackenzie and Marshall state, without giving the evidence, that thio-sulfate reduces arsenate to arsenite in acid solution. We may write the reaction



In alkaline solution the reaction is reversed. We verified the above equation thus. In mols, Solution A originally contained 0.01000  $\text{Na}_2\text{HAsO}_4$ , 0.02000  $\text{Na}_2\text{S}_2\text{O}_3$ , and 0.04000 HCl. After standing for a long time only 0.00080 HCl remained. Solution B originally contained 0.01000  $\text{Na}_2\text{HAsO}_4$ , 0.01500  $\text{Na}_2\text{S}_2\text{O}_3$ , and 0.04000 HCl. The final excess of hydrochloric acid was 0.00892; *i. e.*, 0.03108 HCl has disappeared. If 0.01500  $\text{Na}_2\text{S}_2\text{O}_3$  uses up 0.00750  $\text{Na}_2\text{HAsO}_4$ , 0.00250  $\text{Na}_2\text{HAsO}_4$  remains, which requires 0.00250 HCl to neutralize it. Therefore 0.02858 HCl was consumed in arsenite formation, very nearly the calculated amount.

After standing, solutions of Type A gave a copious and prompt precipitate with hydrogen sulfide as the equation would predict. But silver salts produced a yellow precipitate, rapidly darkening, and barium salts, added to the neutralized solution, an unstable white crystalline precipitate. The last two reactions, highly characteristic of trithionate, suggest the reversible reaction  $\text{H}_3\text{AsO}_3 + \text{S}_4\text{O}_6^{''} \rightleftharpoons 3\text{H}^+ + \text{AsO}_3\text{S}^{''' } + \text{S}_2\text{O}_3^{''}$ . This equilibrium would be displaced from right to left by precipitation of arsenious sulfide, and from left to right by formation of insoluble tri-thionates. The speed of arsenite formation was studied in solutions containing 0.00500  $\text{Na}_2\text{HAsO}_4$ , 0.01000  $\text{Na}_2\text{S}_2\text{O}_3$ , and 0.02000 HCl in 100 cc. At the desired moment reaction was stopped by pouring into a quantity of alkali found by preliminary experiments to be nearly equivalent to the remaining acid. A small amount of standard acid or alkali completed the adjustment. The consumption of acid thus determined was after 15 seconds, 0.00972; 30 seconds, 0.01186; 1 minute, 0.01376; 2 minutes, 0.01504; overnight, 0.01847. The graph was obviously exponential in character, but the above data, before mathematical analysis, require correction at each stage for the quantities of acid hydrogen in the various anions present.

Thiosulfate, therefore, very rapidly reduces arsenate to arsenite, and then converts the latter into arsenious sulfide. These conclusions were confirmed by analysis of the precipitate.<sup>5</sup> The approximate equality of induction periods for arsenate and arsenite, allowing for acid and thio-sulfate consumed in the first stage of the reaction, must follow; for

<sup>5</sup> A brief preliminary statement regarding a part of this work in *Science*, 50, 443 (1919), and *C. A.*, 14, 3605 (1920) requires two corrections. (1) Freezing-point measurements, which we have since made but not recounted here, do not confirm the hypothesis of complex formation; the phenomena are sufficiently explained by the consecutive reactions which occur. (2) Vortmann was incorrectly quoted in the statement made there that arsenic pentasulfide is formed by the action of thiosulfate on arsenate.

a small concentration of arsenite, as shown previously, reacts almost as rapidly as a larger one.

The speed of precipitation of arsenious sulfide from arsenite was next studied (see Table III). To find the amount produced in 30 minutes for instance, the solution stood at 22° for 29½ minutes from the end of the

TABLE III  
PRECIPITATION OF ARSENIOS SULFIDE FROM ARSENITE

Millimoles per liter							
(1) $\text{H}_3\text{AsO}_3$ , 20; $\text{Na}_2\text{S}_2\text{O}_3$ , 200; HAc, 400							
$t$ 1/2	1	2	4	8	16	432	3000
S	6.36	7.11	7.80	8.50	9.63	11.38	16.23
$S_1/S_2$							
Millimoles per liter							
(2) $\text{H}_3\text{AsO}_3$ , 80; $\text{Na}_2\text{S}_2\text{O}_3$ , 80; HAc, 160 m.							
$t$	1	2	4	8	16	404	3000
S	2.32	2.63	2.82	3.18	3.45	6.26	18.0
$S_1/S_2$	3.1	3.0	3.0	3.0	3.3	2.6	1.2

induction period. It was then quickly filtered through a weighed Gooch crucible, the operation consuming one minute. The sulfide was washed, dried at 110°, and after weighing treated with dil. ammonia to prove that free sulfur was absent, or present in traces only. The data are given in millimoles of  $\text{As}_2\text{S}_3/2$ . The course of the reaction suggests autocatalysis, but none of the *final* reaction products, added in small amounts to solutions at the start of their induction periods, changed these materially.

Vortmann's equation calls for 20.0 millimoles of  $\text{As}_2\text{S}_3/2$  from Solution 1, and for  $2/9 \times 80$ , or 17.8 from Solution 2. The excess noted appeared to be due to free sulfur in each case. The precipitation reaction is to some extent reversible, as sulfurous acid dissolves the sulfide perceptibly, but this may be reprecipitated by blowing out sulfur dioxide with a stream of carbon dioxide.

Table IV shows how initial speeds of precipitation vary with concentrations. With acetic acid, speed is almost independent of arsenite, but nearly proportional to thiosulfate and to hydrogen ion concentration. With hydrochloric acid, however, the speed is, roughly, inversely proportional to the latter.

When the ratio of thiosulfate to arsenious acid,  $\text{Na}_2\text{S}_2\text{O}_3/\text{H}_3\text{AsO}_3$ , is 3, initial precipitation is much more rapid if most of the acid is added at the end of the induction period instead of at the beginning. When the ratio is 4, however, no difference is observed. See Table V. In Table VI it is evident that the same change in the ratio, from 3 to 4, strikingly abbreviates the induction period, especially in the more concentrated solutions. An explanation of these highly interesting observations would doubtless throw much light upon the reaction mechanism.

TABLE IV  
INFLUENCE OF CHANGING CONCENTRATIONS UPON MOLES OF  $\text{As}_2\text{S}_3/2$  PRECIPITATED  
IN THE FIRST 15 MINUTES

$\text{H}_3\text{AsO}_3$ Mmoles.	$\text{Na}_2\text{S}_2\text{O}_3$ Mmoles.	HAc. Mmoles.	(H <sup>+</sup> ) Start	$\text{As}_2\text{S}_3/2$ Mmoles.	HCl Mmoles.	$\text{As}_2\text{S}_3/2$ Mmoles.
80	200	400	0.0027	6.46	...	....
40	200	400	0.0027	6.08	400	9.08
20	200	400	0.0027	5.55	400	6.72
20	200	800	0.0038	8.21	800	3.36
20	200	200	0.0019	3.63	200	17.10
20	100	200	0.0019	1.93	200	5.37

TABLE V  
AMOUNT OF ARSENIOS SULFIDE PRECIPITATED IN 15 MINUTES FROM END OF INDUCTION  
PERIOD

Concentrations in millimoles per liter of final mixture						
$\text{H}_3\text{AsO}_3$	80	80	80	80	80	80
$\text{Na}_2\text{S}_2\text{O}_3$	320	320	320	240	240	240
Initial HCl	640	40	40	480	40	40
Added* HCl	0	600	1200	0	440	880
Total HCl	640	640	1240	480	480	920
$\text{As}_2\text{S}_3/2$	12.8	12.6	6.8	9.0	6.7	3.2

\* Added at end of induction period.

TABLE VI  
INFLUENCE OF CONCENTRATION RATIO UPON INDUCTION PERIODS  
 $\text{HCl}/\text{Na}_2\text{S}_2\text{O}_3 = 2$  in all cases

$\text{H}_3\text{AsO}_3$ Mmoles. per liter	Ratio of $\text{Na}_2\text{S}_2\text{O}_3:\text{H}_3\text{AsO}_3$							
	20 Sec.	10 Sec.	5 Sec.	4 Sec.	3 1/2 Sec.	3 Sec.	2 Sec.	1 Sec.
10	180	240	300	600	720	840	1120	1620
20	...	180	180	360	540	720	....	....
40	...	120	120	180	300	600	1110	1350
80	...	65	120	120	210	780	1350	1500
100	...	...	...	120	180	780	1380	1560

### Summary.

The induction period preceding precipitation of arsenious sulfide from an acidified solution containing thiosulfate and arsenite is extremely sharp and reproducible. Its duration is strictly in inverse proportion to thiosulfate concentration, and practically independent of concentration of arsenite, or of acetic acid. Hydrochloric acid prolongs the periods. It is much better for experimental demonstration of induction periods, of the relation between concentration and reaction velocity, and of the temperature coefficient of reaction velocity than the familiar iodine clock.

The prolongation of the periods by strong acids, the limiting concentrations yielding precipitates when arsenates are used, and the speed of precipitation were investigated.

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[CONTRIBUTION FROM THE LABORATORIES OF GENERAL CHEMISTRY, UNIVERSITY OF WISCONSIN]

## EQUILIBRIUM IN THE SYSTEM LITHIUM CHLORIDE:QUINOLINE

BY JAMES H. WALTON AND CLARENCE R. WISE

Received October 31, 1921

In connection with a series of tests on quinoline as a solvent it was found that the solubility of lithium chloride in this substance decreases markedly with rise in temperature. This difference in solubility is sufficient to produce a fairly voluminous crystalline precipitate when a solution saturated at room temperature is heated to the neighborhood of the boiling point. This paper deals with the solubility of lithium chloride in quinoline at various temperatures.

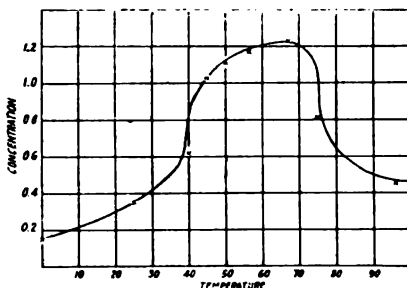
### Experimental

**Reagents.**—The lithium chloride was the purest obtainable on the market. It was purified by recrystallizing from absolute alcohol and drying at  $160^{\circ}$ , and was found free from sodium, potassium, and the nitrate and sulfate ions. Analysis of the chlorine content showed the substance to be 99.8% pure.

The quinoline was dried by allowing it to stand over potassium hydroxide, then over barium oxide, from which it was then distilled. The product obtained in this way was amber colored. To obtain an absolutely colorless liquid at least 6 redistillations were necessary. The colorless product obtained in this way distilled at  $231.4^{\circ}$  at 740.5 mm. The boiling point is given in the literature at  $237\text{--}239^{\circ}$  at 760 mm. On standing in the light, quinoline becomes discolored, but a sample preserved in a bottle coated with asphalt paint showed no change in color after 6 months.

**Apparatus.**—The samples of the liquid phase were taken in an apparatus described by Walton and Judd<sup>1</sup> which permits the sample to be filtered and collected in a weighing bottle without removing it from the constant-temperature bath. Between  $0^{\circ}$  and  $70^{\circ}$  the ordinary type of thermostat was used; above that temperature vapor baths were used, the temperature of the vapors being kept constant by heating them under a pressure that was kept constant by means of an automatic regulator.<sup>2</sup>

**Procedure.**—The dry lithium chloride and quinoline were placed in the tube and stirred until equilibrium was reached, about 48 hours being necessary. Samples of the liquid phase were taken about every 5 hours and the chlorine content determined by the Volhard method. When this was found to be constant a sample was analyzed for chlorine gravimetrically in the usual way. That the presence of quinoline introduces no error in the determination is



<sup>1</sup> Walton and Judd, *THIS JOURNAL*, 33, 1036 (1916).

<sup>2</sup> Mathews and Faville, *J. Phys. Chem.*, 22, 1 (1918).

shown by the following analyses. The sample of lithium chloride was dissolved in 5 cc. of quinoline; 150 cc. of water and an excess of nitric acid were then added.

Sample G.	AgCl G.	LiCl in sample %	LiCl in absence of quinoline %
0.2455	0.8283	99.91	99.79
0.2506	0.8461	99.76	99.79

In analyzing the solid phase the sample was carefully dried with filter paper and then kept in a desiccator until free from adhering quinoline, and the chlorine content determined gravimetrically.

The following table gives the data obtained in these experiments.

TABLE I

SOLUBILITY OF LITHIUM CHLORIDE IN QUINOLINE

Temperature °C	LiCl per 100 g. of solvent G.	LiCl in solid phase %
0	0.1515	13.92
25	0.3538	13.97
40	0.6175	13.43
45	1.0328	13.90
50	1.1107	14.30
56.4	1.1734	14.22
67	1.2353	14.23
75	0.8180	14.14
96	0.4588	14.33

The composition of the solid phase corresponds to the formula  $(C_9H_7N)_2 \cdot LiCl$ , containing 14.1% of lithium chloride. This compound is very stable at all temperatures between 0° and 97°. A sample standing in a desiccator for 2 weeks showed no change in composition.

Above 67° the length of time necessary to bring about equilibrium resulted in decomposing the quinoline. As a consequence the analyses above this temperature become less accurate. There is evidence of the formation of a new solid phase above 100°, but because of reasons just mentioned its composition was not determined.

The results obtained are shown graphically in the figure. That we have here a single curve and not the intersection of two curves is conclusively proved by the constant composition of the solid phase.

### Summary

1. The solubility of lithium chloride in quinoline has been studied between 0° and 97°.
2. The solid phase in equilibrium with the lithium chloride-quinoline solution has the composition, between 0° and 97°, of  $(C_9H_7N)_2 \cdot LiCl$ . This compound has never been reported before.
3. The decomposition of quinoline makes it impracticable to study the solubility above 97°.

MADISON, WISCONSIN

[CONTRIBUTION FROM THE BUREAU OF STANDARDS, U. S. DEPARTMENT OF COMMERCE.]

## EQUILIBRIA IN THE SYSTEMS CARBON DISULFIDE:METHYL ALCOHOL, AND CARBON DISULFIDE:ETHYL ALCOHOL.<sup>1</sup>

By E. C. MCKELVY AND D. H. SIMPSON.<sup>2</sup>

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### Introduction.

The occasion for the determination of the data presented in this paper arose several years ago in connection with work on the preparation of pure anhydrous alcohols to be used in density determinations. As is well known, in certain cases of limited miscibility between two liquid components, the critical solution temperature offers an extremely sensitive criterion of the purity or of changes in purity of either compound provided that the other component is either pure or of constant composition.

Mixtures of hydrocarbons, such as gasoline and kerosene, have been used extensively in testing the lower alcohols, but in order to obtain a fixed and easily reproducible point it is desirable to have a definite compound as the second component. Various hydrocarbons of the methane series, such as pentane, hexane or heptane, could be used for this purpose, but they are difficult to prepare with a sufficient degree of purity. Carbon disulfide is preferable because it is easily prepared pure and is fairly stable when kept under the proper conditions. It therefore appeared that more work should be done and more reliable values obtained on the equilibria in such common systems, of which the boiling-point curves have been the subject of study by many investigators.

### General Principles.

The present discussion of equilibria in binary systems in which the components are only partially miscible will be confined to temperatures at which the vapor pressures of the components are small, far less than the critical pressures, and to cases in which only the upper critical solution temperature is realizable.

Consider two components such as A and B (Fig. 1) which are not completely miscible in the liquid state. Small quantities of B added to A, at the temperature  $T_c$ , will at first dissolve forming a homogeneous liquid phase. When the liquid has the composition represented by the point  $a$ , further quantities of B will not dissolve, but will take up some A from

<sup>1</sup> Published by permission of the Director of the Bureau of Standards, Washington, D. C.

<sup>2</sup> This investigation was practically completed prior to the death in November, 1919, of Mr. McKelvy, the senior author, and the manuscript was subsequently prepared by the junior author. Valuable suggestions were received from Mr. G. W. Morey, of the Geophysical Laboratory.



the liquid, forming a second liquid layer of composition  $b$ . As more and more B is added, the phase  $b$  will increase in amount, while the conjugate

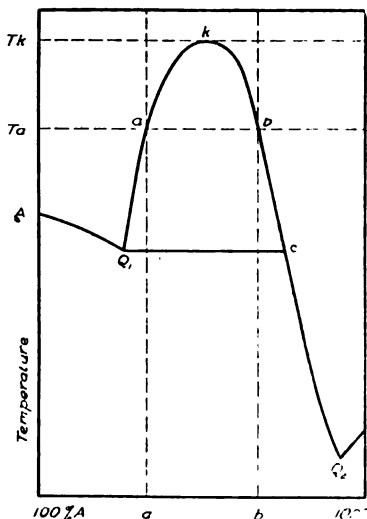


Fig. 1.—Typical equilibrium diagram for two partially miscible components.

solution  $a$  will decrease until when the mass has the composition  $b$  the first liquid will have disappeared completely. Similarly, if the liquid A be added to B at the temperature  $T_a$ , the mixture will remain homogeneous until the composition  $b$  is reached, when a second liquid layer of the composition  $a$  will separate.

As the temperature is changed the mutual solubility of the two liquids will change, the solubility increasing if the differential heat of solution is negative, decreasing if it is positive. We will consider the case that the solubility in each layer increases with temperature. The two conjugate liquids  $a$  and  $b$  will then approach each other in composition, until at the “critical solution temperature”  $T_k$ , the two solutions become identical in composition, and the curve has a horizontal tangent. At temperatures above the critical solution temperature the two components are completely miscible in the liquid state.

The effect of the introduction of a third component into a binary system exhibiting limited miscibility will depend on whether the added substance increases or decreases the mutual solubility of the two liquids. Consider a ternary system ABC (Fig. 2) in which the components A and B are partially miscible;  $K$  is the binary critical solution,  $a$  and  $b$  two binary conjugate liquid layers at a lower temperature  $T_a$ . If addition of C increases the mutual solubility of  $a$  and  $b$ , the two liquid layers will approach each other in composition, until at  $K'$  they become identical;  $T_a$  is the ternary critical solution temperature of the mixture of composition  $K'$ . Addition of C in this case lowers the critical solution temperature. The case in which addition of C diminishes the mutual solubility is shown in Fig. 3; the two curves  $aa'$

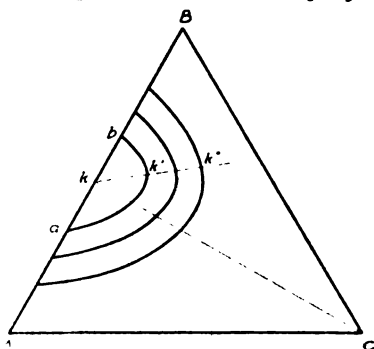


Fig. 2.—Three component system, in which addition of C increases the mutual solubility of A and B.

Fig. 3; the two curves  $aa'$

and  $bb'$  give the composition of the two liquid layers at the temperature  $T_c$ . In this case a higher temperature is necessary in order to make the two layers miscible, and addition of C will raise the critical solution temperature. Both the direction of the effect and its magnitude depend on the specific properties of the components; the first case will usually be found in systems in which the component C is miscible with both A and B, the second case in systems in which the component C is immiscible with either A or B, or with both. In the latter case the effect will be the more marked the more complete the immiscibility. An example is the effect of water on the critical solution temperature of the system ethyl alcohol-kerosene, in which 1% of water raises the critical solution temperature nearly  $20^\circ$ .

The effect of addition of the component C on the ratio A/B of the conjugate solutions and the critical solution should also be considered.

Addition of C will in general alter the proportion of A and B in the conjugate solutions (Fig. 2), and the curve passing through the critical compositions will not in general coincide with the curve KC, which represents the compositions of the solutions obtained by adding C to the binary critical mixture K. In other words, when increasing amounts of C are added to the mixture represented by the point K, the temperature at

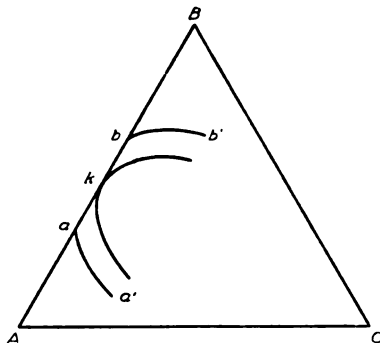


Fig. 3.—Three-component system, in which addition of C decreases the mutual solubility of A and B.

which the liquids become mutually soluble is not the critical temperature, but merely a point on the mutual solubility surface of the ternary system. At the critical solution temperature, on the curve  $KK'K''$  the two liquid phases become identical in composition; at a point on the line KC, a liquid of one (changing) composition becomes completely soluble in another of different (changing) composition. This distinction between points on the line KC and between true critical solution temperatures is one often disregarded.

### Earlier Work.

Study of the earlier work showed wide discrepancies in values, which are probably almost totally ascribable to impurity of the materials used.

1. In the system carbon disulfide: methyl alcohol, Rothmund<sup>3</sup> obtained  $39.92^\circ$  as the critical solution temperature and approximately 84.5% by weight of carbon disulfide as the critical concentration. Timmermanns<sup>4</sup> in a very comprehensive paper

<sup>3</sup> Rothmund, *Z. physik. Chem.*, 26, 433 (1898).

<sup>4</sup> Timmermanns, *Récherches Expérimentales sur les Phénomènes de Démixion des Mélanges Liquides. Thesis*, University of Brussels, 1911.

reported 48.5° for the critical solution temperature of this system but gave no value for the concentration. He stated that the alcohol used contained traces of water. No values could be found in the literature for temperatures below zero.

2. In the system carbon disulfide:ethyl alcohol Guthrie<sup>5</sup> gave -14.4° for the critical solution temperature. No value for the critical concentration can be read from a curve through the four points given by him. Kuenen<sup>6</sup> gave -10.6° for the critical solution temperature, but no values for concentration. For this system values have been found for only five concentrations, probably because of the low temperature required for the complete investigation.

### Purification of Materials.

The materials used were carefully purified and special attention was paid to the dehydration of the alcohols. Freezing points, densities, and the critical solution temperature itself were used as criteria of purity. (Hereafter the abbreviation c. s. t. will be used in place of the words critical solution temperature.)

**Carbon Disulfide.**—Preliminary tests were made in which samples were purified as follows: (a) by treatment with bromine; (b) by treatment with fuming nitric acid, one portion being further treated with phosphorus pentoxide and another portion with conc. sulfuric acid; (c) by distillation from a flask containing ceresin. The c. s. t. of each sample (see Table I) with the same test alcohol was used as a basis for comparing the different products.

TABLE I  
PRELIMINARY TESTS ON CARBON DISULFIDE

Treatment	C. s. t. with test alcohol No. 1 C
Bromine	35.27
Fuming HNO <sub>3</sub>	
(a) then P <sub>2</sub> O <sub>5</sub>	34.99
(b) then H <sub>2</sub> SO <sub>4</sub>	35.00
Distilled from ceresin	35.00

The carbon disulfide used was prepared by the third method which seemed to be simple as well as efficient. No satisfactory explanation has been offered of the mechanism by which the ceresin removes the impurities. Twelve liters of technical carbon disulfide was distilled from about 900 g. of ceresin. The middle fractions of this distillation were combined and redistilled from fused calcium chloride. The temperature of the vapor remained constant at 46.6° (uncorr.) during both distillations. The constancy of the c. s. t. of the fractions as shown in Table II indicates that the second distillation might not have been necessary.

Fraction 5 of the second distillation was used in this investigation. Its freezing point was determined as follows.

<sup>5</sup> Guthrie, *Phil. Mag.*, [5] 18, 495 (1884).

<sup>6</sup> Kuenen, *Phil. Mag.*, [6] 6, 637 (1903).

TABLE II  
FINAL PURIFICATION OF CARBON DISULFIDE

Distilled from Ceresin Fraction	C. s. t. with test alcohol No. 2 °C	Fractions 2 to 6 combined and distilled from CaCl <sub>2</sub> Fraction	C. s. t. with test alcohol No. 3
1	34.15	1	34.80
2	34.80	2	34.78
3	34.75	3	34.65
4	34.70	4	34.75
5	34.60	5	34.65
6	34.90	.	.....

The carbon disulfide was first frozen by means of liquid air in a bulb to which was attached by a glass-to-metal joint<sup>7</sup> a diaphragm valve through which the bulb was connected to the freezing-point apparatus, illustrated in Fig. 4. The valve was then opened and after the entire system had been evacuated the carbon disulfide was melted and condensed into the freezing-point tube. During the measurement of the freezing point the liquid was stirred with a platinum stirrer fastened to a gold-plated iron ring which in turn was moved up and down by a large permanent magnet outside. Temperatures were measured by means of a platinum resistance thermometer<sup>8</sup> which extended into the carbon disulfide. The freezing point obtained was  $-112.0^{\circ}$ , which agrees with that given by Henning<sup>9</sup> ( $-112.0^{\circ}$ ) as the mean of 17 determinations on different samples.

This thermometer was standardized in ice, steam and sulfur vapor, in the customary way, the temperatures being calculated by the Callendar formula. Below  $-40^{\circ}$ , temperatures calculated by this formula are too low, and the calculated temperatures were corrected to the hydrogen scale, using the deviation curve found by Henning.<sup>9</sup> Since the platinum used in this thermometer was of the same high purity as that used by Henning, the use of his correction curve could introduce no significant error, especially since the total correction at the lowest temperature measured ( $-112^{\circ}$ ) amounts to only  $0.3^{\circ}$ .

**Methyl Alcohol.**—Preliminary drying of the methyl alcohol was accomplished by distillation from lime, but the last traces of water were removed by treatment with sodium, since when lime was used for the final dehydration, great swelling of the lime occurred and loss of alcohol resulted. Two distillations from sodium were necessary before a constant composition was obtained as shown by the constant c. s. t. of the fractions with a test gasoline. (See Table III).

The second fraction of the third distillation was used in this work. Its

<sup>7</sup> McKelvy and Taylor, *THIS JOURNAL*, 42, 1364 (1920).

<sup>8</sup> *Bur. of Standards Bull.*, 6, 154 (1909).

<sup>9</sup> *Henning, Ann. Physik.*, 40, 653 (1913).

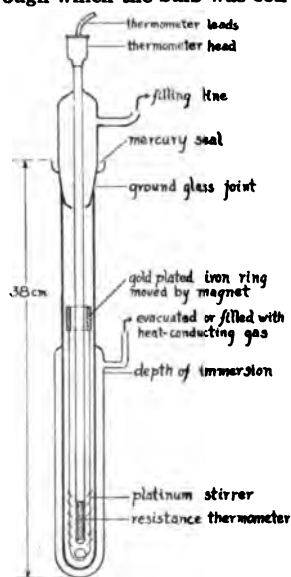


Fig. 4.—Freezing-point apparatus.

density ( $d_4^{25}$ ) was 0.78658 and its freezing point  $-97.7^\circ$ . Timmermann's<sup>10</sup> value for the melting point is  $-97.1^\circ$  and Young's<sup>11</sup> value for  $d_4^{20}$  is 0.7915 and for  $d_4^{30}$  is 0.7825.

**Ethyl Alcohol.**—This alcohol was originally prepared from ivory nuts, which source gives a product especially free from aldehydes. It was dehydrated by prolonged refluxing with fine freshly calcined lime. A slow stream of dry air was passed through the very top of the condenser and the condenser water was kept at about  $55^\circ$ . By this means the alcohol was condensed, but aldehydes, if present, passed through and were swept away. Constancy of the c. s. t. as shown in Table IV with a test kerosene oil was the criterion of constant composition of the fractions.

TABLE III

FINAL PURIFICATION OF METHYL ALCOHOL

Third distillation from sodium Fraction	C. s. t. with test gasoline °C.
1	29.68
2	29.49
3	29.48
4	29.47

TABLE IV

FINAL PURIFICATION OF METHYL ALCOHOL

Fourth distillation from lime Fraction	C. s. t. with test oil No. 5 °C.
1	23.30
2	23.23
3	23.11
4	23.00
5	22.95
6	23.00

Fraction 5 of the fourth distillation was used in this work. Its density ( $d_4^{25}$ ) was 0.78506, which is identical with the value previously determined at this Bureau.<sup>12</sup>

### General Description of Apparatus and Methods.

**Temperature Baths.**—For ordinary temperatures a water-bath was used. It consisted of an inverted bell jar provided with an efficient stirrer, a steam heating-coil and a cold water cooling-coil. The low-temperature bath consisted of a 500cc. Dewar cylinder fitted with a stirrer and a cooling coil into which liquid air could be siphoned in small quantities. Petroleum ether was used for the contact liquid because it can be cooled to  $-125^\circ$  before it freezes or becomes cloudy. In using this type of bath every possible precaution must be taken to avoid introducing liquid air directly into the bath itself, and to avoid mixing the vapors from the bath liquid with those from the liquid air, especially as the latter may be nearly pure oxygen. Care must also be taken to eliminate as far as possible any means such as sparks from motors, frictional electricity, etc., which might ignite the vapors. Neglect of these precautions

<sup>10</sup> Timmermann, *Proc. Roy. Soc. Dublin N. S.*, 13, 339 (1912).

<sup>11</sup> Young, *ibid.*, 12, 374 (1910).

<sup>12</sup> *Bur. Standards, Bull.*, 9, 327 (1913).

may cause serious trouble. The death of Mr. McKelvy,<sup>13</sup> the senior author, resulted from an explosion while working with a bath of this type. The exact cause of this explosion is unknown.

**Temperature Measurements.**—Temperatures in the water-bath were measured with a mercury thermometer. The low temperatures were measured with a single-junction copper-constantan thermocouple, using a potentiometer of the White type.

The wire used for this thermocouple was taken from a stock of B. and S. gage No. 36 wire (0.127 mm. diam.) which was known to be exceedingly homogeneous, different couples made from this stock differing in their indications by less than 1 part in 1000. Two 10-junction thermocouples made from this wire had been calibrated by comparison with platinum-resistance thermometers. These platinum resistance thermometers had been standardized to reproduce the scale of Henning's hydrogen thermometer.<sup>14</sup> The results of the intercomparisons with the platinum-resistance thermometers, and a separate measurement at the freezing point of mercury, were in agreement within 0.02° with those given by the empirical equation, for a single junction

$$E = 38.836t + 0.04576t^2 - 0.00004243t^3$$

where  $E$  is e. m. f. in microvolts, and  $t$  is the temperature in centigrade degrees, the cold junction of the couple being at 0°.

It seems probable that the single junction couple used could, by means of the equation given, be used to reproduce the scale of Henning's hydrogen thermometer with an accuracy of a few hundredths of a degree down to -40°, and to within 0.1° at the lowest temperatures, (-112°) reached in the measurements given in this paper.

**Procedure.**—All determinations were made with the mixtures contained in glass bulbs of about 5 cc. capacity blown at the end of a short piece of tubing. Preliminary data were obtained with cork-stoppered bulbs, the liquids being measured from burets.

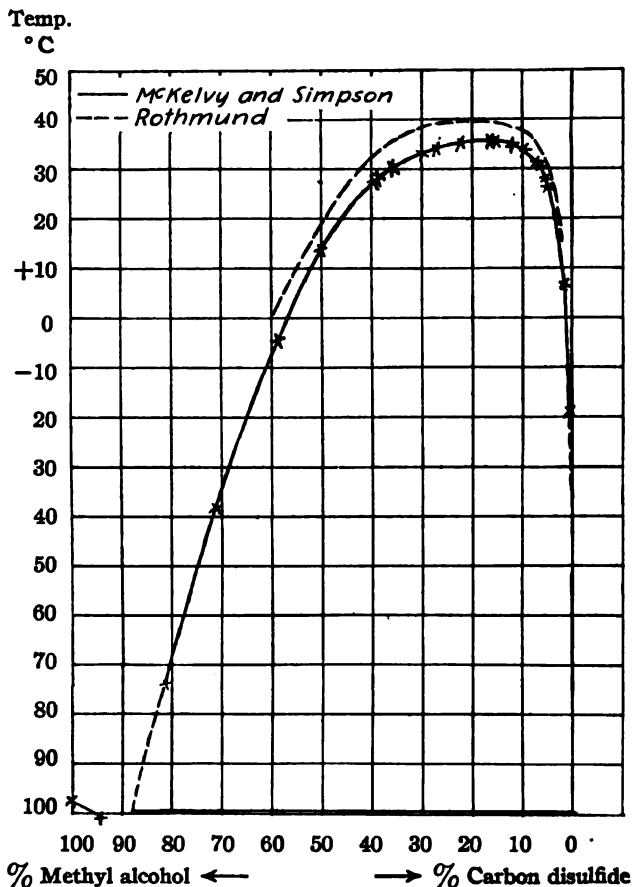
Mixtures for the final measurement were made by a different method, using bulbs fastened to valves by glass-to-metal joints. The alcohol and carbon disulfide were contained in long graduated bulbs (burets) also attached to the line by metal valves. The bulb to contain the mixture was fastened to the line and the whole system evacuated. By immersing the bulb in liquid air any desired amount of either liquid was distilled over. With the valves and unions used the bulb could be detached, weighed and again attached repeatedly without change in weight, as shown by McKelvy and Taylor.<sup>7</sup> The system was again evacuated and after the liquid in the bulb was frozen the valves were opened and the desired amount of the other component distilled over. After weigh-

<sup>13</sup> McKelvy, *J. Ind. Eng. Chem.*, 12, 94 (1920).

<sup>14</sup> Henning, *Ann. Physik.*, 40, 635 (1913); 43, 282 (1914).

ing the bulb the mixture was again frozen in liquid air and the tube sealed as close as practicable to the bulb. It is to be noted that by this method, which excluded contact with air and moisture, the liquids received a final distillation not long before the c. s. t. was determined.

The temperature of complete mutual solubility, or the unmixing temperature, of any mixture can be found by noting either the temperature



• Fig. 5.—Temperature of complete mutual miscibility of mixtures of carbon disulfide and methyl alcohol.

at which the cloudiness of the mixture disappears when shaken in a bath whose temperature is gradually rising, or the temperature at which cloudiness appears when the temperature of the bath is falling. The temperature of the bath was changed so slowly that the bulb was considered to be at the same temperature as the bath. In the systems studied the opalescence is so great that it obscures the clouding point, especially by the first method. By the second method, when the bulb is shaken with

a swirling motion a cloudy wisp appears and is followed immediately by complete cloudiness. Trials were made to determine the clouding point by looking through the bulb at a scale immersed in the bath, and also looking directly at a light suspended behind the bath.

The procedure finally adopted was as follows. Having found approximately the mutual solubility temperature while warming the bath, the accurate readings were made when the temperature was falling very slowly. By looking directly at the light the formation of the cloudy wisp

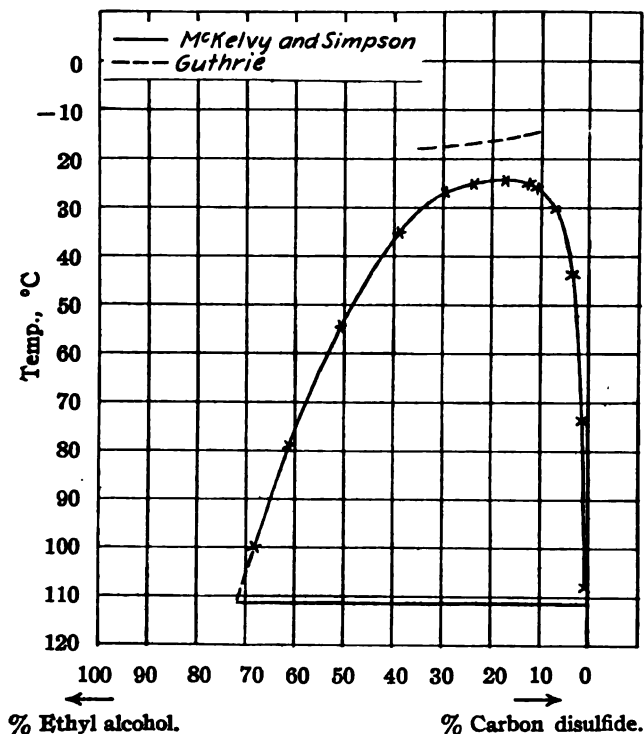


Fig. 6.—Temperatures of complete mutual miscibility of mixtures of carbon disulfide and ethyl alcohol.

could be observed, even through the troublesome opalescence. The temperature at which the wisp appeared was considered to be the true unmixing temperature and successive determinations on the same mixture were constant to  $0.01^\circ$  or  $0.02^\circ$ . The determinations on different mixtures are presented in Tables V and VI and Figs. 5 and 6. The critical solution temperature and composition were interpolated from these data.

#### Discussion of Results.

**Carbon Disulfide : Methyl Alcohol.**—The c. s. t. of this system is  $35.7^\circ$



and the critical concentration is approximately 85% by weight of carbon disulfide.

The temperature at which solid methyl alcohol separates from the alcohol-rich layer is  $-99.6^{\circ}$ . This corresponds to temperature  $Q_1$  of Fig. 1; the compositions of the two conjugate solutions  $Q_1$  and  $c$  were not determined. The unmixing temperature of a solution containing only 0.36% of methyl alcohol is  $-18.95^{\circ}$ , and the liquid  $c$  would be at even smaller methyl alcohol concentration; the binary eutectic  $Q_2$  would contain even less alcohol. More complete study of mixtures rich in carbon disulfide was prevented by the accidental destruction of the low-temperature bath.

TABLE V  
TEMPERATURES OF COMPLETE MUTUAL MISCIBILITY OF MIXTURES OF CARBON DISULFIDE AND METHYL ALCOHOL

CS <sub>2</sub> %	Unmixing temperature °C.	CS <sub>2</sub> %	Unmixing temperature °C.	CS <sub>2</sub> %	Unmixing temperature °C.
99.64	-18.85	88.43	34.82	61.03	28.60
98.47	+ 6.46	84.73	35.75	60.53	27.34
95.27	26.50	83.89	35.63	49.93	+13.80
94.74	28.00	77.65	35.30	41.29	- 4.43
93.55	30.58	72.85	34.09	28.78	-38.37
93.40	31.08	70.13	33.35	18.70	-73.60
90.22	33.80	64.12	30.70	6.39	Freezes at -100.7°

**Carbon Disulfide:Ethyl Alcohol.**—The c. s. t. of this system is  $-24.4^{\circ}$  and the critical concentration is approximately 83% by weight of carbon disulfide. The temperature at which all mixtures freeze is  $-111.7^{\circ}$ . Since the freezing point of carbon disulfide is  $-112^{\circ}$ , the solid phase is probably this substance, and the eutectic lies on the ethyl alcohol side. In this system carbon disulfide corresponds to component A and ethyl alcohol to component B. The composition of the two co-existing liquid phases at the quadruple point  $Q_2$  was not determined. On the alcohol side complete study of the curve was impossible because of vitreous solidification.

TABLE VI  
TEMPERATURES OF COMPLETE MUTUAL MISCIBILITY OF MIXTURES OF CARBON DISULFIDE AND ETHYL ALCOHOL

CS <sub>2</sub> %	Unmixing temperature °C.	CS <sub>2</sub> %	Unmixing temperature °C.	CS <sub>2</sub> %	Unmixing temperature °C.
99.09	-108.04	87.48	-25.07	61.23	-35.17
98.55	-73.68	82.71	-24.31	49.46	-54.58
96.78	-43.71	76.25	-25.13	38.75	-79.26
93.05	-30.16	70.39	-26.88	31.96	-100.07
89.57	-25.76	.....	.....	.....	.....

Applications of the above data have not been worked out. McKelvy<sup>16</sup>

<sup>16</sup> McKelvy, Ref. 12, pp. 330-370.

has confirmed the results of earlier investigators on the estimation of small amounts of water in ethyl alcohol by its effect on the critical solution temperature of a test kerosene. The effect of water on the critical solution temperatures of methyl alcohol-carbon disulfide and of ethyl alcohol-carbon disulfide mixtures could be similarly applied to the estimation of water in methyl or ethyl alcohol, and would offer the advantage of making use of a definite compound instead of an indefinite mixture of hydrocarbons such as kerosene. It has been found that the addition of 1% of water raises the c. s. t. about  $10^{\circ}$ . As early as 1871,<sup>16</sup> the possibility of determining the purity of ethyl alcohol by measuring the solubility of carbon disulfide in it at a fixed temperature (*e. g.*,  $17^{\circ}$ ) was pointed out, and suitable equations were derived. This method is not, however, as sensitive as the measurement of the c. s. t. By using the proper components the c. s. t. method can be used for testing products in many processes. In fact, Orton and Jones<sup>17</sup> have reported on c. s. t. as a criterion of purity of organic liquids of industrial importance.

### Summary.

Earlier work on the critical solution temperature of carbon disulfide with methyl and ethyl alcohol is reviewed. Methods of purification of these substances are given, and a freezing-point apparatus is described.

A detailed description is given of the method used in preparing the mixtures for critical solution temperature measurement.

The values obtained are as follows.

	Crit. sol. temp. $^{\circ}$ C	Crit. concentration % CS <sub>2</sub>
Carbon disulfide : methyl alcohol	35.7	85
Carbon disulfide : ethyl alcohol	-24.4	83

Some applications of the critical solution temperature are suggested.

WASHINGTON, D. C.

<sup>16</sup> Tuschmidt and Follenius, *Ber.*, **4**, 583 (1871).

<sup>17</sup> Orton and Jones, *J. Chem. Soc.*, **115**, 1194 (1919).

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA.]

**EQUILIBRIUM IN THE REACTION BETWEEN SULFUR DIOXIDE AND WATER.**

By F. RUSSELL BICHOWSKY.

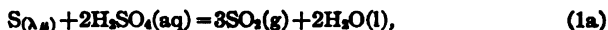
Received November 1, 1921.

As far back as 1775, Priestley discovered that sulfur dioxide heated with water in a sealed tube decomposes, giving sulfur and sulfuric acid according to the reaction,<sup>1</sup>



This reaction which is still but little known is reversible, the reverse reaction being the basis of a familiar method of preparing sulfur dioxide. Since measurements of the equilibrium constant for this reaction would, when combined with existing data, give material for the calculation of the free energy of formation of aqueous sulfuric acid, and since, taken in connection with the projected measurements of Randall of the free energy of the reactions  $2\text{Hg}(l) + 2\text{H}_2\text{SO}_4(aq) = \text{Hg}_2\text{SO}_4(s) + \text{SO}_2(g) + 2\text{H}_2\text{O}(l)$  and  $\text{H}_2(g) + \text{Hg}_2\text{SO}_4(s) = 2\text{Hg}(l) + \text{H}_2\text{SO}_4(aq)$  they would give a valuable check on the value for the free energy of formation of sulfur dioxide, it was decided to investigate the equilibrium in this reaction quantitatively.

Preliminary experiments showed that in very dilute sulfuric acid the reverse reaction



is complicated by the side reaction<sup>2</sup>



This reaction takes place quantitatively when sulfur is treated with a large excess of water in a fused silica tube. Thus 0.1603 g. of sulfur heated with 18.0 g. of water in a fused silica tube for 60 days to approximately 260° gave 0.1220 g. of sulfuric acid ( $\text{H}_2\text{SO}_4$ ) (calc. 0.1226 g.), and 0.1250 g. of hydrogen sulfide (calc. 0.1278 g.). A trace of sulfur dioxide was present. This reaction is reversible; 20 cc. of 6 *N* sulfuric acid was heated with 0.1022 g. of hydrogen sulfide for 10 days at 250°; 0.112 g. of sulfur was found (calc. 0.1282 g.) and 0.095 g. of sulfur dioxide showing that reaction 1a had to a small extent taken place simultaneously with Reaction 2.

In order to prevent side Reaction 2 it was decided to use fairly concentrated acid and as high temperatures as practicable. Sulfur in excess was therefore heated in small silica tubes of known volumes, with a known

<sup>1</sup> Ordinary molten sulfur is, as is well known, a mixture of  $\text{S}_\lambda$  (soluble sulfur) and  $\text{S}_\mu$  (insoluble sulfur), and perhaps other species. By  $\text{S}(\lambda_\mu)$  is meant the equilibrium mixture of  $\text{S}_\lambda$  and  $\text{S}_\mu$ . Cf. Kruyt, *Z. physik. Chem.*, **64**, 513 (1908).

<sup>2</sup> For preliminary investigations on this reaction and other reactions of sulfur, see Lewis, Randall and Bichowsky, *THIS JOURNAL*, **40**, 356 (1918).

amount ( $1/3$  the volume of the tube) of sulfuric acid of the strength desired. At the temperature used ( $312^\circ$ ) even Pyrex glass is rapidly attacked by sulfuric acid, wherefore the use of silica tubes. At this temperature, moreover, the total pressure in the tube is in the neighborhood of 150 atmospheres. The tube had therefore to be protected from bursting by being enclosed in a steel bomb partially filled with water, in order to counterbalance the pressure inside and outside the small silica tubes. At the end of 12 days (other experiments showed that equilibrium was not reached in 3 days but was in 7) the bomb was cooled and opened and the sulfur dioxide content of the silica tubes determined by breaking them under standard iodine solution and titrating back with thiosulfate. The results are given in Table I; Col. 1 gives the weight concentration of the acid used (mols. per 1000 g. of solution), Col. 2 the amount of acid (solution) in g. introduced into the tube, Col. 3 the volume of the tube in cc., Col. 4 the amount of iodine used, in mols. It is possible, assuming that the only reaction taking place in the tube was 1a, by a laborious calculation, the details of which will not be given, to determine the total pressure of sulfur dioxide (Col. 5) present at equilibrium, and also the concentration of sulfuric acid and water at equilibrium. From these data, using the methods of the latter part of this paper, the equilibrium constants for the reaction  $2\text{H}_2\text{SO}_4(N=0.101) + \text{S}_{(\lambda)} = 3\text{SO}_2(\text{g}) + 2\text{H}_2\text{O}$  were calculated and are given in Col. 6.

TABLE I  
PRELIMINARY EQUILIBRIUM CONSTANTS

$\text{H}_2\text{SO}_4$ $M$	Wt. G.	Vol. Cc.	$\text{I}_2$ $M$	$P_{\text{SO}_2}$ (Atm.)	$K_p \times 10^{-11}$
2.120	1.006	3.018	0.00198	48.6	5.5
	1.040	3.443	0.00205	41.1	2.3
	0.873	2.944	0.00172	40.7	2.1
	0.952	3.229	0.00191	40.6	1.7
	0.836	3.339	0.000653	13.0	4.9
	0.806	3.643	0.000660	11.4	3.9
0.947	0.874	3.504	0.000631	12.0	2.9
	1.238	3.383	0.000284	7.2	11.2
	0.995	3.139	0.000248	6.3	14.5
	1.179	4.383	0.000392	6.4	28.0
	0.925	3.277	0.000244	5.5	9.9

This constant varies greatly and does not agree with that found by our later method using more concentrated acid. Therefore it may be concluded that for acids of this strength Reaction 2 cannot be neglected, although experiments showed it possible, under proper conditions, to cool our tubes rapidly enough so that both hydrogen sulfide and sulfur dioxide could be detected. It was felt that the danger of the reaction  $2\text{H}_2\text{S} + \text{SO}_2 = 2\text{H}_2\text{O} + 3\text{S}$  taking place at appreciable amount during cooling was too great to warrant further experiments with acids of these concentrations.

covered by the cooling jacket being deeply threaded to provide extra cooling surface. Just below the part of the bomb which was in the furnace were cut two deep V-shaped grooves Bd. These, by reducing the thickness of the metal in this, the sharpest part, of the temperature gradient, greatly reduced the heat leak without much decreasing the strength of the tube. The small tube Bn was simply screwed down in shellac on a seat Bo. This joint was permanent and so does not require the more elaborate devices which were necessary for the constantly re-opened joint Dd. In this joint the cone Bp which is brazed on the end of the tube Bn, is made with a taper about 5 degrees less than the seat De, so that when forced home by screwing up the vanadium-steel nipple Dd the tip of Bp is sprung against the seat in such a way that any liquid pressure in the tube tends to seat Bp still more tightly. Such joints, when properly constructed, can be made and remade time after time without the slightest leak. The unions at Db and Dc are similar. The pump used in the apparatus was simply an old screw-plunger pump with a special sliding (rather than turning) steel and leather plunger packing. This pump was seated on an aluminum washer protected by shellac. To make unnecessary the very special precautions that are needed to hold a sliding contact against mercury a thin layer of heavy oil was placed on top of the mercury. With this precaution this simple pump showed no leak at 200 atmospheres. The tube Dc was also filled with oil to protect any brass in the gage from the mercury.

With such an apparatus as this with which the heat leak is so very large, the problem of designing a thermostat, keeping the upper end of the bomb at 300° while the lower end is kept cold, is no light one. The thermostat must have large heating capacity, the minimum of temperature lag, and the greatest possible heat conductivity, the heat leak being mostly at one point where the bomb enters the thermostat.

To meet these requirements the thermostat was made of a heavy casting of aluminum Ca in which had been cast the steel bulb Cg and stem Ch of the temperature regulator. The heating was done with two coils of Nichrome wire wound on a thin coating of an insulating cement and protected with the same material. In order to counterbalance in some degree the temperature gradient down the bomb an auxiliary heating coil Bm was wound in cement on the upper portion of the bomb itself. This auxiliary coil fitted tightly in the space Cd of the furnace. The temperature of the furnace was read by two thermometers Cc and Cb which fitted closely into two holes bored for that purpose into the aluminum casting. The whole furnace was insulated by 25 mm. of asbestos-magnesia mixture Cf placed between the tin jacket Cm and the casting. As such a thermostat consumed a total of about 3 kilowatts at the higher temperatures, almost  $\frac{1}{3}$  of which must pass through the regulating coil, the design of the make-and-break for the relay is a matter of some interest. The wipe contact, long-armed relay set shortly to be described by Randall, meets this demand nicely. However, to make this instrument work, enough current must be sent through the mercury make-and-break to cause it to arc badly. Moreover, mercury in an iron regulator at this temperature seems to become foul rapidly even with no sparking. To avoid these difficulties it was decided to keep an atmosphere of hydrogen over the mercury. For this reason the small automatic electrolytic hydrogen generator, shown at Ek, connected in parallel with the spark, was made continuous with the other glass parts of the regulator. It is advisable, though not necessary, to have a small plug of glass wool at Ef to prevent spray and to have the connections of the 2 arms of the U-tube somewhat constricted to prevent sudden gurgitation. With this apparatus the usual platinum wire at Ee can be replaced by Nichrome. A rubber stopper at Eg makes a satisfactory seal. Fine regulation can be made by sliding the wire in the stopper, and

coarse by withdrawing or adding mercury through Eb. Phosphoric acid will be found the best electrolyte for this miniature hydrogen generator as for most others. It does not stick to the walls and form short circuits as potassium hydroxide is apt to do, nor does it give off sulfur dioxide at the electrode as sulfuric acid may do, nor does its vapor react with mercury as hydrochloric acid does. With such an apparatus, a mercury contact will keep clean indefinitely even with heavy sparking.

It is of course important that an apparatus of this sort be filled very carefully and that no air or moisture be trapped in it. For these reasons it was found desirable to fill the apparatus in a vacuum. To do this the reaction tube A was removed from the bomb and connected through a 2-way stopcock to the vacuum line and to an evacuated vessel containing boiled-out sulfuric acid of the strength desired. After thoroughly evacuating the quartz apparatus, a process which could be accelerated by heating, enough sulfuric acid was introduced to fill the apparatus completely, and the tube then removed from the pump. The apparatus was then inverted and mercury poured in to fill Ah. The mercury could not run into the other parts of the tube because of the trap Af. The quartz tube was then carefully dried on the outside and placed in the bomb, which was then tightly sealed, evacuated, and filled with mercury. The joint Dd was then quickly made but not completely screwed up, and the bomb placed in the proper inclined position. The joints were then all tightened and pressure applied from E to test for leaks. The furnace was then put in place and rapid heating begun, the lower end of the apparatus, of course, being cooled with running water. After the apparatus had reached the

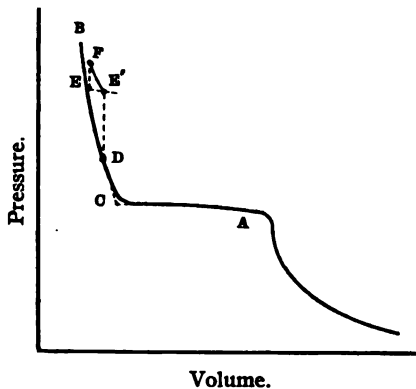


Fig. 3.—Pressure-volume isotherm.

required temperature, pressure-volume isotherms were made; that is to say, the volume of the apparatus was changed by means of the calibrated pump and the pressure read corresponding to the various volumes. If heating had been done so rapidly that but little sulfur dioxide had time to form, the isotherm obtained was the regular  $P$ - $V$  isotherm for sulfuric acid (Fig. 3), the portion of the curve from C to A representing the vapor pressure of the acid at various volumes of the system, the portion from B to C representing, when corrected for, a compressibility of the mercury and cold sulfuric acid and for the dilation of the instrument, the change of pressure of the hot liquid sulfuric acid for a given change of volume. The slight slope of the portion of the curve C to A, *i. e.*, the slight variation of the vapor pressure with the total volume of the system is due to the evaporation of the water into the varying gas space above the sulfuric

acid, changing the concentration of the acid. Ideally BC and AC should join at a sharp angle if no sulfur dioxide had time to form or if no gas was trapped in the system due to faulty filling. In this case the pressure corresponding to the point C would be the vapor pressure of the sulfuric acid in contact with zero gas space, and hence of the concentration initially introduced. Practically there was always a slight curvature at C, but its position could be approximated by extrapolating the straight parts of BC and AC until they crossed.

Having thus obtained the preliminary isotherm, the pressure was set a little above the probable vapor pressure (Point D, Fig. 3) of the acid and the reaction allowed to proceed. Equilibrium was usually reached in a couple of days (for temperatures about  $300^{\circ}$ ), pressure going up to say E. The volume of the apparatus was then changed the pressure increasing to say F (Fig. 3). Now without changing the volume the heating was continued and we would find, the pressure F being above equilibrium, that the pressure would fall to E'. Thus equilibrium could be approached from both sides; moreover, since the point E' could be so chosen as to lie as nearly as desired to the curve CB, equilibrium could be obtained with but zero gas space. Thus no appreciable change of concentration of the acid was possible. Moreover, it will be noted that in the cases where the mol. fraction of sulfur dioxide is  $\frac{1}{2}$  that of water, the composition of the acid (as is approximately the case in Expts. 6, 7 and 8) is independent of the gas space, no matter how large that may be.

By means of this procedure it was possible to obtain measurements approaching equilibrium from both sides, which would check, except at the highest pressures, to within one atmosphere.

Table II gives the results of some preliminary experiments in which the vapor pressure of sulfuric acid of several strengths was determined either in the absence of sulfur, or in the presence of sulfur before the sulfur dioxide had time to be formed. In this table the first column gives the number of the experiment, the second the mol fraction  $N_{\text{H}_2\text{SO}_4}$  of sulfuric acid, the third the absolute temperature, and the fourth the pressure,  $p'_{\text{H}_2\text{O}}$  in atmospheres.<sup>4</sup> The measurements with pure water were made to test the method and the results agree closely with those obtained by other observers. As the temperature approaches the critical temperature of water the difficulty of determining the vapor pressure becomes greater owing to the difficulty of finding a flat portion of the pressure-volume isotherm, but if care be taken to eliminate all foreign gas these difficulties are reduced to a minimum. In Expt. 1 sulfur was present and only one point was determined before sulfur dioxide began to form; Expts. 2, 3 and 4 were made in the absence of sulfur; Expts. 5 and 6 with sulfur present, according to the method outlined.

<sup>4</sup> The gas phase is essentially pure water vapor.

TABLE II  
VAPOR PRESSURES OF SULFURIC ACID

Expt.	$N_{H_2SO_4}$	$T$	$p_2$
1 S	0.160	540	30
2	0.101	588	84
3	0.101	543	45
4	0.101	496	19.5
5	0.101	593	95
6	0.101	563	58
7	0.0	498	25.5
8	0.0	563	72
9	0.0	612	141

The results for the equilibrium measurements are given in Table III. The first column gives the absolute temperature  $T$ ; the second the mol. fraction of the sulfuric acid; the third the total pressure  $P_E$  of water vapor, sulfur vapor and sulfur dioxide; the fourth the pressure of water vapor from sulfuric acid of the strength given, in the absence of sulfur dioxide.<sup>5</sup>

TABLE III  
EQUILIBRIUM MEASUREMENTS

Col. 1	2	3	4	5	6	7	8
$T_{abs.}$	$N_{H_2SO_4}$	$P_E$	$P_{H_2O}$	$\log f_{H_2O}$	$\log \alpha_{H_2SO_4}$	$\log \alpha_{H_2SO_4}^{P_E}$	$\log f_{H_2O}^{P_E}$
1	613	0.041	185	138	2.05	-3.04	2.06
2	585	0.041	114	96	1.89	-2.98	1.90
3	561	0.101	90	59	1.71	-1.34	1.71
4	598	0.101	197	98	1.92	-1.55	1.94
5	588	0.101	166	85	1.86	-1.50	1.88
6	537	0.160	84	28	1.41	-0.54	1.42
7	572.5	0.160	185	49	1.65	-0.85	1.68
8	562	0.160	150	42	1.58	-0.76	1.60
9	527	0.363	190	...	....	.....	....
Col. 9	10	11	12	13	14	15	
$\log f_{H_2O}$	$N_{SO_2}$	$\frac{P_E}{V_{SO_2}}$	$\log f_{SO_2}$	$\log f_{SO_2}^{P_E}$	$\log K_P$	I	
1	2.13	(0.13)	(196)	2.14	(1.26)	(13.6)	(125.5)
2	1.94	(0.10)	(336)	2.03	(1.02)	(12.2)	(126.8)
3	1.84	0.25	410	1.87	1.27	10.11	124.5
4	2.08	0.27	172	2.15	1.58	12.21	124.0
5	2.03	0.29	202	2.09	1.55	11.68	124.3
6	1.78	0.57	414	1.84	1.59	8.87	126.7
7	1.97	0.49	166	2.11	1.80	10.89	124.4
8	1.93	0.52	205	2.04	1.76	10.32	125.1
9	....	....	...	....	....	.....	....
Mean						124.5	

<sup>5</sup> The experimental part of this paper was completed in June 1916, while working under the direction of G. N. Lewis, to whom the author wishes to express his gratitude. Preliminary calculations of the equilibrium constant were made by Dr. Lewis and the author at that time. The present calculations are a complete revision of these earlier ones.



Before proceeding to an explanation of the remaining columns in Table III, we must point out the extraordinary difficulties attending the calculation of the equilibrium constant. If measurements could have been carried on at low pressures and temperatures, and if sulfuric acid were a perfect solution the equilibrium constant for the reaction  $S + 2H_2SO_4 = 2H_2O + 3SO_2$  would be of course simply

$$K_p = \frac{[H_2O]^2[SO_2]^3}{(H_2SO_4)^2}$$

where the quantities in brackets are pressures and  $(H_2SO_4)$  is the mol fraction of  $H_2SO_4$ ,  $[H_2O]$  the vapor pressure of water over sulfuric acid of the strength used (*i. e.*, the measured vapor pressure of sulfuric acid), and  $[SO_2]$  the difference between the vapor pressure of the sulfuric acid and the total measured equilibrium pressure. However, in our actual case the gases and solution are so imperfect that more elaborate methods are necessary.

**The Calculation of the Fugacity of Water.**—The equation for the equilibrium constant written above is, however, still exact if instead of using the pressures and concentrations of the substances involved we use their fugacities and activities. Now the pressure  $P$  of any gas is related to the fugacity  $f$  at any temperature and pressure by the equation

$$RT \ln \frac{P}{f} = \int_0^P (v' - v) dp, \quad (1)$$

where  $v'$  is the molal volume of a perfect gas,  $v$  that of the actual gas, and the integral from zero pressure to the pressure in question gives the area between the isotherm of a perfect gas and that of the actual gas<sup>6</sup> for the temperature and pressure used.

For water vapor the compressibility has been accurately determined at various temperatures and pressures, and the results are represented with fair accuracy by the equation of state given by Linde,<sup>7</sup> which for one mol becomes in terms of atmospheres, liters and absolute temperatures,

$$Pv = 0.0823T - p(1 + 0.0206P) \left( \frac{29050000}{T^2} - 0.0948 \right). \quad (2)$$

Combining (1) and (2), and integrating, we find

$$RT \ln \frac{P}{f} = p(1 + 0.0103) \left( \frac{29050000}{T^2} - 0.948 \right). \quad (3)$$

This equation allows us to calculate from the measured pressure of water over the sulfuric acid, at any temperature, the fugacity of the water at that temperature and pressure.

<sup>6</sup> Lewis, *Proc. Am. Acad.*, 37, 49 (1901); *Z. physik. Chem.*, 38, 205 (1901).

<sup>7</sup> Linde, *Ver. deut. Ing. Forschungsarb.*, Berlin, 21, 33 (1905); *Z. Ver. deut. Ing.*, 49, 1745 (1905).

Now the close agreement between the measurements on the vapor pressure of the acid made in the presence of sulfur and sulfur dioxide (Table II) and those made in the absence of sulfur and sulfur dioxide justifies us in assuming that sulfur and sulfur dioxide are not sufficiently soluble in our acid at the temperatures and pressures used to affect the activity of the water in the solution. Therefore we may assume that the values for the fugacity of water calculated from the vapor pressure of the water over the sulfuric acid will be the same (excepting for a small correction due to the compression of the aqueous acid by the excess pressure of sulfur dioxide) whether sulfur dioxide is present or absent. Hence in order to calculate the fugacity of water in our mixture all that is needed is the vapor pressure of the acid at our concentration and temperatures. For these vapor pressures we have, in the first place, our measurements (Table II) and, secondly, at lower temperatures, *i. e.*, 184.5° and 218°, unpublished values<sup>8</sup> of the vapor pressure of sulfuric acid of various strengths, due to Randall and James, and at still lower temperatures the measurements of Burt,<sup>9</sup> Briggs,<sup>10</sup> Tammann,<sup>11</sup> Sorel,<sup>12</sup> Regnault,<sup>13</sup> Brönsted,<sup>14</sup> and Dieterici.<sup>15</sup> Using these values, a plot was made giving the best values of the logarithm of the vapor pressure against the reciprocal of the absolute temperature for various concentrations of acid. The values  $P_{H_2O}$  for our concentrations and temperatures read off this plot are given in Col. 4 of Table III.  $\log f_{H_2O}$ , calculated from Equation 3 is given in Col. 5.<sup>16</sup>

There is, however, another method of obtaining the fugacity of the water over the sulfuric acid at our temperatures. The fugacity change is connected by means of the equation

$$\Delta F = RT \ln \frac{B}{f_A} \quad (4)$$

with the free energy change of a process which consists of taking a mol. of

<sup>8</sup> These values are:  $T=184.4^\circ$ ;  $N=0.1509$ ,  $p=5.72$ ,  $N=0.2101$ ,  $p=3.84$ ,  $N=0.2795$ ,  $p=2.25$  for  $T=218.0^\circ$ ;  $N=0.1509$ ,  $p=12.01$ ,  $N=0.2101$ ,  $p=7.85$ ,  $N=0.2795$ ,  $p=4.87$ ,  $N=0.300$ ,  $p=4.20$  (pressures in atmos., concentrations in mol. fractions). Quoted by permission.

<sup>9</sup> Burt, *J. Chem. Soc.*, **85**, 1339 (1904).

<sup>10</sup> Briggs, *J. Soc. Chem. Ind.*, **22**, 1375 (1903).

<sup>11</sup> Tammann, *Mém. Acad. Pétersbourg* [7] **35**, (1885), quoted from Landolt-Börnstein-Roth "Tabellen," 1912, p. 427.

<sup>12</sup> Sorel, *Z. angew. Chem.*, **2**, 272 (1889).

<sup>13</sup> Regnault, *Ann. chim. phys.*, [3] **15**, 179 (1845).

<sup>14</sup> Brönsted, *Z. physik. Chem.*, **68**, 708 (1909-10).

<sup>15</sup> Dieterici, *Wied. Ann.*, **42**, 513 (1891); **50**, 47 (1893); **62**, 616 (1897).

<sup>16</sup> Due to an accident in the last of the experiments with sulfuric acid of mol. fraction 0.363 the vapor pressure of water was not obtained and there seems to be no way of estimating this pressure with any degree of certainty. No measurements were made on the vapor pressure of the most dilute acid, but here interpolation from the results at higher concentration can be used with some confidence.

any substance from the state A to the state B. Our process is the reaction  $\text{H}_2\text{O}(\text{g}) = \text{H}_2\text{O}(\text{in } \text{H}_2\text{SO}_4)$ , which is more conveniently treated as the sum of the processes (a)  $\text{H}_2\text{O}(\text{g}) = \text{H}_2\text{O}(\text{l})$ , and (b)  $\text{H}_2\text{O}(\text{l}) = \text{H}_2\text{O}(\text{in } \text{H}_2\text{SO}_4)$ . The free energy change in Reaction a may be calculated from data given by Lewis and Randall from the equation

$$\Delta F = -13259 - 9.21T \ln T - 0.00097T^2 + 0.00000037T^3 + 90.20T^{.17}$$

The free energy change in Process b, *i. e.*, the partial free energy of solution of water in various strengths of sulfuric acid, may be calculated at  $25^\circ$  from the vapor pressure of the acid at that concentration and temperature, where, assuming that water vapor at these low pressures (less than 25 mm.) is a perfect gas, we may substitute pressures in place of fugacities, in Equation 4, and obtain the equation

$$\Delta F = RT \ln \frac{P_{\text{H}_2\text{O}}}{P^\circ_{\text{H}_2\text{O}}},$$

$P_{\text{H}_2\text{O}}$  being the measured vapor pressure of water over sulfuric acid, and  $P^\circ_{\text{H}_2\text{O}}$  the vapor pressure of pure water, *i. e.*, 23.8 mm. The best values for the vapor pressure of water over sulfuric acid at  $25^\circ$  are those of Brönsted<sup>14</sup> and of Regnault.<sup>15</sup> These agree well enough except at our highest concentration, where unfortunately neither value is consistent with the value obtained by indirect methods from freezing-point determinations, and where apparently there is no way of estimating  $\Delta \bar{F}_{298}$ . The values for  $\Delta \bar{F}$  for Process b for our other concentrations are given in Col. 2, Table IV. Col. 1 of this table gives the corresponding concentration of the acid expressed in mol fractions of sulfuric acid.

TABLE IV  
FREE ENERGY CHANGES

$N$	$\Delta \bar{F}_{298,0}$	$\Delta \bar{H}_{298,0}$	$\Delta \bar{T}_0$	$\Delta \bar{H}_0$	$i_0$
0.0411	-71	-27	-0.32	+66	-2.28
0.101	-296	-282	+0.68	-479	+4.49
0.160	-615	-686	-0.68	-489	-4.30
0.363	.....	-2570	-6.37	.....	.....

In order to obtain  $\Delta \bar{F}_{\text{H}_2\text{O}}$  at other temperatures we must know  $\Delta \bar{H}_{\text{H}_2\text{O}}$ , the partial molal heat of solution of water in sulfuric acid of our concentrations, and the change of that quantity with the temperature. Rümelin<sup>18</sup> has measured  $\Delta \bar{H}_{\text{H}_2\text{O}}$  directly at  $17^\circ$ , and the same quantity may be calculated from data on the integral heat of solution of water given by Brönsted.<sup>19</sup> The values of  $\Delta \bar{H}_{290}$  obtained by drawing the best smooth curve through these values are given in Table IV, Col. 3. The values for  $\bar{c}_{p,\text{H}_2\text{O}}$  (the partial molal heat capacity of water in solutions of sulfuric acid)

<sup>17</sup> Lewis and Randall, *THIS JOURNAL*, **36**, 980 (1914). We have arbitrarily taken the heat capacity of water as 18.01 at all temperatures. This value cancels out.

<sup>18</sup> Rümelin, *Z. physik. Chem.*, **58**, 449 (1907).

<sup>19</sup> Brönsted, *Ref. 14*, Table 12. Recalculation is necessary.

are calculated, using the method of intercepts,<sup>20</sup> from the measurements of Biron<sup>21</sup> on the specific heat of sulfuric acid : water mixtures. The values obtained for  $\Delta\bar{T}_{\text{H}_2\text{O}}$ , again assuming that  $C_p$  for pure water is 18.01 are given in Col. 4, Table IV. Values of  $\Delta\bar{H}_0$  and  $I$  obtained by the usual methods, assuming  $\Delta\bar{T}_{\text{H}_2\text{O}}$  constant, are given in Cols. 5 and 6, respectively, of this table. The values of  $\Delta\bar{H}_0$ ,  $\Delta\bar{T}_{\text{H}_2\text{O}}$  and  $I$  for the reaction  $\text{H}_2\text{O}(\text{g}) = \text{H}_2\text{O}(\text{in } \text{H}_2\text{SO}_4)$  are simply the sum of the  $\Delta\bar{H}_0$ 's,  $I$ 's, etc., for Equations  $a$  and  $b$ . We may therefore calculate the fugacity of the water for the various concentrations and temperatures used in these experiments. The values calculated are consistent both with the data of Randall and James and our own data, and within the limit of error, *i. e.*, 1% of those directly estimated in Table III.

These fugacities are, however, still subject to a slight correction due to the fact that the dissolved water is not under its own vapor pressure, but under the total pressure  $P_E$ . The effect of pressure on fugacity is given by the equation

$$\left(\frac{\partial \ln f}{\partial P}\right)_T = \frac{\bar{v}}{RT}, \quad (7)$$

where  $\bar{v}$ , the partial molal volume of water dissolved in sulfuric acid, may be calculated at 25°, using the method of intercepts, from the very accurate data on the density of sulfuric acid solutions given by Domke and Bein.<sup>21</sup>

For the temperatures of these experiments  $\bar{v}$  may be approximated by assuming that at all temperatures the ratio of  $\bar{v}$  to the density of pure water is constant. The values of fugacity of water so corrected are given in Col. 8, Table III.

**Activity of Sulfuric Acid.**—The standard state for sulfuric acid will be taken as hypothetical molal, *i. e.*, the state in which  $a_2/N_2 = 1$ .<sup>22</sup> Lewis and Randall<sup>23</sup> have given a table of the activity coefficients for sulfuric acid extending to a concentration of 20 molal ( $N = 0.26$ ). Unfortunately no way seems available for extending this table to  $N = 0.363$ . The values for  $\Delta F$ , for the reaction  $\text{H}_2\text{SO}_4(M) = \text{H}_2\text{SO}_4(\text{actual})$ , calculated from the

TABLE V

$N$	$\Delta\bar{F}_{298}$	$\bar{L}_{298}$	$\Delta\bar{H}_{298}$	$\bar{C}_{P298}$	$\Delta\bar{T}$	$\bar{H}_0$	$I$
0	— $\infty$	—20600	0	10.21	0	.....	.....
0.0411	— 982	—16370	+ 4230	27.65	17.25	— 770	97.6
0.101	+1995	—12930	+ 7670	14.71	4.31	+6420	9.72
0.160	+4330	—10500	+10100	22.45	12.05	+6605	60.96
0.363	.....	— 4600	+16000	38.63	28.22	+7820	.....

<sup>20</sup> Lewis and Randall, *THIS JOURNAL*, 43, 237 (1921).

<sup>21</sup> Biron, *J. Russ. Phys. Chem. Soc.*, 31, 190 (100). Data reproduced, Domke and Bein, *Z. anorg. Chem.*, 43, 143 (1905).

<sup>22</sup> Ref. 20, p. 244.

<sup>23</sup> Lewis and Randall, *THIS JOURNAL*, 43, 1128 (1921).

equation  $\Delta F = 3RT \ln (jm^{4/3})$ , are given for our concentrations (Col. 1) and for the temperature  $T = 298$  (Col. 2) in Table V.

The values of  $\bar{f}_{290} = \bar{H} - H^\circ$  (Col. 3, Table V) have been recalculated from data given by Brönsted, the value for infinitely dilute sulfuric acid ( $N=0$ ) being estimated by extrapolation. The values for  $\bar{c}_p(\text{H}_2\text{SO}_4)$  (Col. 4, Table V) are calculated from the same data used for  $\bar{c}_p(\text{H}_2\text{O})$ . By special treatment of the data for dilute solutions,  $\bar{c}_p$  for infinitely dilute solutions was found to be 10.21. The values of  $\Delta \bar{H}_{290}$ ,  $\Delta \bar{F}$ ,  $\bar{H}_0$  and  $I$  are calculated in a manner entirely analogous to that used for water, and the results are given in Table V, Cols. 6, 7 and 8, respectively. In order to calculate  $\Delta F$  at the temperatures of our experiments, we have to make some assumption as to the change of  $\Delta \bar{F}$  with the temperature. We have no data on this point. However, the fact that the fugacity of water, calculated in an analogous manner, assuming  $\Delta \bar{F}_{\text{H}_2\text{O}}$  constant, gave values so near the experiment justifies us in assuming  $\Delta \bar{F}_{\text{H}_2\text{SO}_4}$  constant. On these assumptions, substituting in the appropriate values of the constants from Table V, we have calculated the activity of sulfuric acid at the temperature of our experiments. The values of  $\alpha_{\text{H}_2\text{SO}_4}$  are given in Table III, Col. 6. These values, like those for the fugacity of water, must be corrected for the effect of the excess pressure, in this case the total pressure  $P$ . Corrected values are given in Table III, Col. 7. It will be noted that in one case the activity of sulfuric acid changes 0.12% per atmosphere added pressure.

**Fugacity of Sulfur Dioxide.**—It now remains to calculate the fugacity of the sulfur dioxide. If sulfur dioxide and water vapor were both perfect gases it would suffice to subtract from the measured equilibrium pressure the corrected pressure for water, plus the vapor pressure of sulfur (negligible in all experiments), the remainder being the partial pressure of sulfur dioxide. However, neither sulfur dioxide gas nor water vapor is a perfect gas at our temperatures and pressures. Thus in one case the vapor pressure of water is 98.0 atmospheres and its fugacity (the thermodynamically equivalent perfect gas pressure) is 83 atmospheres, while in the case of sulfur dioxide the assumption of the perfect gas laws would give 99 atmospheres, while the value we are about to calculate is 38 atmospheres. Other methods are therefore necessary. Unfortunately very little is known about the equation of state of mixed gases. However, Lewis and Randall have assumed, with considerably plausibility,<sup>24</sup> that just as mixtures of liquids, where the molecules are far apart and where there are no polar forces, are likely to form perfect solutions, the activity of each constituent being proportional to its mol fraction, so gas mixtures in which the molecules are many times further removed, and where polar forces are still less, are still more likely to form perfect solutions. If this

<sup>24</sup> Unpublished Treatise on Thermodynamics.

is the case we may apply the equation for a perfect solution,<sup>25</sup> *i. e.*,

$$f = f_0 N, \quad (8)$$

where  $f_0$  is the fugacity of the pure substance at the temperature and total pressure of the mixture,  $N$  the mol fraction, and  $f$  the desired fugacity of the desired constituent in the mixture. In applying this equation to our case, we may first consider the water. Here we have Equation 3 already used connecting fugacity and pressure. To find  $f_0$  therefore we merely have to solve for  $f$  in this equation at the total equilibrium pressure  $P_E$ . Of course actually pure water vapor could not remain a vapor at certain of the temperatures and total pressures used. Thus in Case 7 pure water has a vapor pressure of only 84.0 atmospheres; at pressures above this water would condense into a liquid, the fugacity remaining essentially constant. But just as in certain liquid mixtures in which the law of perfect solutions holds we are compelled to treat them as if they were mixtures, one of the components of which is a supercooled liquid, so here we may treat our water vapor as a supercooled gas, and, applying our equation, find the values of  $f^\circ_{\text{H}_2\text{O}}$  given in Table III, Col. 9. It is perhaps worthy of note that in Case 7 the fugacity  $f^\circ_{\text{H}_2\text{O}}$  is only 93.4 atmospheres, while the total pressure is 185.0 atmospheres. Having found  $f^\circ_{\text{H}_2\text{O}}$  we may divide through by the values of  $f^\circ_{\text{H}_2\text{O}}$  corrected for pressure and obtain  $N_{\text{H}_2\text{O}}$ , the mol fraction of  $\text{H}_2\text{O}$ . The mol fraction of  $\text{SO}_2$ , given in Col. 10, Table III, is obviously  $1 - N_{\text{H}_2\text{O}}$ . (The small vapor pressure of sulfur may be neglected.) Now knowing the mol fraction of sulfur dioxide we may find the actual fugacity of sulfur dioxide by reversing our procedure for water. Unfortunately, however, we have no experimental information about the equation of state for sulfur dioxide extending to our pressures and temperatures.<sup>26</sup> We may however assume that at corresponding states it is the same as that of carbon dioxide. For the temperature and pressure interval corresponding to those in which we are interested the equation of van der Waals, *i. e.*,  $(p - a/v^2)(v - b) = RT$ , holds satisfactorily for carbon dioxide if we use the values of  $a$  and  $b$  calculated from critical data. We may therefore assume the same equation for sulfur dioxide, using as values of the constants  $a$  and  $b$  those calculated from the critical constants in the usual manner. We shall take as the critical pressure of sulfur dioxide 77.65 atmospheres, and as the critical temperature  $430.24^\circ \text{K}$ . Using these values,  $a$  and  $b$  are found to be for one mol of gas, 6,775,000 and 56.9, respectively. It may be shown that for a gas which obeys van der Waals' equation the fugacity is given by the equation,

$$\log f = \log \frac{RT}{(v-b)} + \frac{1}{2.3026} \left( \frac{b}{v-b} - \frac{2a}{RTv} \right). \quad (9)$$

<sup>25</sup> Lewis, *Proc. Am. Acad.*, 43, 265 (1907).

<sup>26</sup> The data by Roth, *Wied. Ann.*, 11, 1 (1880), extend only to  $T = 456.3$ .

For our temperatures and total pressures  $P_E$ ,  $v$  may be found by solving van der Waals' equation. The values found are given in Table III, Col. 11. Substituting these values of  $v$  in Equation 9 gives  $f^{\circ}_{\text{SO}_2}$ . These values are given in Table III, Col. 12. These values multiplied by the mol fraction give the actual fugacity,  $f_{\text{SO}_2}$  (Table III, Col. 13) of the sulfur dioxide. Finally the equilibrium constant for the reaction  $\text{S}_{(\lambda)} + 2\text{H}_2\text{SO}_4(M) = 3\text{SO}_2(g) + \text{H}_2\text{O}(g)$  is given by the equation  $\log K_p = 3 \log f_{\text{SO}_2} + 2 \log f_{\text{H}_2\text{O}} - 2 \log a_{\text{H}_2\text{SO}_4}$ , the values of  $\log K_p$  so calculated being given in Table III, Col. 14.

**Heat of Reaction.**—In order to calculate the equilibrium constant at  $25^\circ$  we must know the heat of the reaction as well as the specific heats of the constituents. Apparently the best values for the heat of formation of sulfur dioxide gas are those of Berthelot.<sup>27</sup> Excluding the third series, the mean of his values is 69,390,<sup>28</sup> at  $18^\circ$ .

The direct values for the heat of solution of sulfur dioxide gas are not concordant. Thomsen<sup>29</sup> measured the heat  $\text{SO}_2(l) = \text{SO}_2(aq)$ ;  $N = 0.00320$ ;  $N = 0.00205$  and found  $\Delta H_{291} = 1444$ ; 1564. Taking  $\Delta H_{291} = 5370$  for the reaction  $\text{SO}_2(l) = \text{SO}_2(g)$ ,<sup>30</sup> we find for the heat of the reaction  $\text{SO}_2(g) = \text{SO}_2(aq)$ ;  $N = 0.00205$ ;  $\Delta H = 6935$  cal. This is in close agreement with the corresponding values for  $\Delta H$  calculated from data<sup>31</sup> on the vapor pressure of sulfurous acid solutions at various temperatures and concentrations. We shall take  $\Delta H = 6950$  for the concentration used by Thomsen in the experiments about to be mentioned. The heat of the reaction  $\text{Cl}_2(aq) + \text{SO}_2(aq) + 2\text{H}_2\text{O} = \text{H}_2\text{SO}_4(aq) + 2\text{HCl}(aq)$  has been measured by Thomsen<sup>29</sup> for  $\text{H}_2\text{SO}_4$  of the mol fractions 0.000286, 0.000507, 0.000536. The values for  $\Delta H$  given are  $-74320$ ,  $-73780$ ,  $-73620$ , respectively. Correcting to infinite dilution, these become  $-75120$ ,  $-75200$ ,  $-75090$ , respectively; average,  $-75140$ . The best value for  $\Delta H_{291}$  for the reaction  $\text{Cl}_2(g) + \text{H}_2(g) = 2\text{HCl}(aq)$ ;  $N = 0$  is  $-78400$ .<sup>32</sup> The best value for the heat of formation of  $\text{H}_2\text{O}(l)$  at  $18^\circ$  is 68330.<sup>17</sup> The best value for the heat of vaporization of water at  $18^\circ$  is  $\Delta H = +10525$ .<sup>17</sup>  $\Delta H_{291}$  for the reaction  $\text{S}_r = \text{S}_\lambda$  will be taken as  $+350$ .<sup>33</sup>

<sup>27</sup> Berthelot, *Ann. chim.*, [5] 22, 428 (1881).

<sup>28</sup> For a discussion of this value see Ferguson, *THIS JOURNAL*, 40, 1626 (1918).

<sup>29</sup> Thomsen, "Thermochemische Untersuchungen," Leipzig, 1882, vol. II, p. 250.

<sup>30</sup> Mathias, *Compt. rend.*, 106, 1149 (1888).

<sup>31</sup> Linder, *Monatsh.*, 33, 645 (1912). Calculated  $\Delta H$  for the concentrations of 0.000534; 0.00234; 0.01212; 0.03750 g.  $\text{SO}_2$  per cc. are 9130; 7700; 6970; 6680, respectively. The value directly measured by Thomsen,<sup>29</sup> *i. e.*,  $\Delta H = 7700$  cc. for 1 mol. of  $\text{SO}_2$  to 250 mols. of  $\text{H}_2\text{O}$ , is apparently in error due to some analytical trouble. Berthelot's (*Ann. chim.*, [VI] 1, 74 (1884)) value,  $\Delta H_{291} = 8.34$  for  $\text{SO}_2(g) = \text{SO}_2(aq)$ ; 13.3 g. per liter is somewhat less in error due to the same reason. Berthelot's values for heat of dilution of aqueous sulfurous acid (84 g. per liter) with 5 volumes of water, namely  $\Delta H_{291}$  280, is, however, consistent with that calculated from Linder.

<sup>32</sup> Ref. 17, p. 1977.

Therefore for the reaction  $S_\lambda + 2H_2SO_4(aq) = 3SO_2(g) + 2H_2O(g)$   $\Delta H_{298} = +95450$ . The heat capacity of the various substances involved will be taken as  $C_p(S_\lambda) = 5.4 + 0.05T$ ;<sup>33</sup>  $C_p(H_2SO_4, M) = 10.2$ ;<sup>34</sup>  $C_p(SO_2, g) = 7.0 + 0.0071T - 0.00000186T^2$ ;<sup>35</sup>  $C_p(H_2O, g) = 8.81 - 0.0019T + 0.00000222T^2$ .<sup>36</sup> From these data  $\Delta F$  may be calculated as  $\Delta F = 12.80 + 0.0125T - 0.00000114T^2$ ;  $\Delta F$  for any temperature is therefore given by the equation

$$\Delta F = +91205 - 12.8T \ln T - 0.00625T^2 + 0.00000019T^3 + 17. \quad (10)$$

This is for the reaction  $S_\lambda + 2H_2SO_4(M) = 3SO_2(g) + 2H_2O(g)$ . The reaction actually measured differs from this in that  $S_{(\lambda\mu)}$  was used instead of  $S_\lambda$ . Lewis and Randall<sup>33</sup> have given a table for  $\Delta F$  for the reaction  $S_\lambda = S_\lambda$  at various temperatures which allows us to correct our measured values of  $\Delta F$  in order to use equation 10. Having  $\Delta F$  at our temperatures we may calculate  $I$ , the values determined being given in Table III, Col. 15. Using the mean of these values, we may calculate  $\Delta F$  for 298° for the reaction  $S_\lambda + 2H_2SO_4(M) = 3SO_2(g) + 2H_2O(l)$ , the value found being +31500.

It is difficult to say how much this value may be in error. The most serious source of error seems to be the uncertainty in the heat of formation of sulfuric acid and sulfur dioxide. These values may readily be in error by  $\pm 2000$  cal. The next most serious source is the arbitrary assumption that  $\Delta F$  for sulfuric acid is constant over the temperature range employed. This assumption is probably not correct but it would be even more arbitrary to make any other in the absence of further data. The error introduced here may be as much as  $\pm 1000$  cal. The experimental errors which are likely are the effect on the fugacity of the sulfuric acid and water of the solubility of sulfur dioxide, which we have neglected, and an effect on the concentration of the sulfuric acid due to the same cause. Errors due to uncertainty of temperature and pressure readings and due to thermodynamic data and methods employed other than those mentioned above, are almost certainly not over 500 cal. The two measurements made with acid of the mol fraction 0.041 are subject to another source of error, namely, the side reaction  $2H_2O(g) + 3S_{(\lambda\mu)} = SO_2(g) + 2H_2S(g)$ . The amount of correction due to this source can be calculated, and the bracket values in Table III have been corrected by this amount, assuming best values for  $\Delta F$  for sulfur dioxide and hydrogen sulfide. This correction should be negligible at the higher concentrations. Excepting this correction, the probable sources of error are such that the above value for  $\Delta F$  is too low if anything.

### Summary.

The reactions of liquid sulfur with aqueous sulfuric acid have been studied

<sup>33</sup> Lewis and Randall, *THIS JOURNAL*, 33, 476 (1911).

<sup>34</sup> Table V.

<sup>35</sup> Lewis and Randall, *THIS JOURNAL*, 36, 1133 (1912).

<sup>36</sup> Ref. 35, p. 1132.



over a wide range of conditions. At low concentrations of sulfuric acid two reactions take place simultaneously, namely, (1)  $S_{(g)} + 2H_2SO_4(aq) = 2H_2O(l) + 3SO_2(g)$  and (2)  $4S_{(g)} + 4H_2O(l) = 3H_2S(g) + H_2SO_4(aq)$ . These reactions are both reversible. In the acids of higher mol fraction than 0.05, and at temperatures up to the critical point of water, Reaction 2 becomes negligible. Equilibrium pressures for Reaction 1 have been measured for acids of mol fraction ranging from 0.041 to 0.363, and at temperatures ranging from 527°A to 613°A, using a new type of apparatus. The vapor pressures of various concentrations of sulfuric acid have been measured with the same apparatus. Using these and other existent data, the free energy for the reaction  $S_{(g)} + 2H_2SO_4(M) = 2H_2O(g) + 3SO_2(g)$  has been calculated to be +31500 cal. at 25° and standard conditions. From these and other data the free energy of both aqueous sulfuric acid and sulfur dioxide may be calculated.

A new type of apparatus for measuring equilibrium or vapor pressures of corrosive liquids up to high pressures and temperatures has been described.

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## QUANTITATIVE ANALYSIS BY CENTRIFUGE.

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Chemical investigators in the domains of biology, medicine and soil analysis have ever sought for rapid methods of experiment and analysis. In these sciences experimental deviations are so great that one must greatly increase the number of samples for analysis in order to get reliable results.<sup>1</sup> Speed rather than great precision is needed in such cases; one needs methods less precise than those which he would employ where the conditions more constant. Accordingly we have in text-books many rapid methods; for example, the colorimetric, the nephelometric, etc.

Curiously enough very little use is made, in such rough quantitative researches, of direct readings of the volume of the precipitate, although this is a very common method in the so-called mechanical analysis of soils. This method attains its greatest accuracy when the columns of precipitate are compressed by means of centrifugal force. In the dairy and in clinical technique the centrifuge has been much used, but it is rarely used for quantitative work in the inorganic laboratory. Nevertheless, the centrifugal method can be used with considerable accuracy. For example Hedin<sup>2</sup> succeeded in determining very satisfactorily the

<sup>1</sup> For example Waynicke points out that from an area as small as half an acre, one must collect over 80 samples for analysis, in order to get a moderately accurate result. (*Univ. Cal. Publ. Agr. Sci.*, 3, 1918.)

<sup>2</sup> Hedin, *Skand. Arch. f. Physiol.*, 5, (1895).

osmotic pressure of different solutions by means of plasmolyzing blood corpuscles and then reading off the compressed columns in capillary stems. The attempts which have been made to use the centrifugal method for more usual analytical purposes have never been crowned with great success, probably because of an arbitrarily chosen time for centrifuging and because the tubes employed have not been suitable for the purpose. The first experimenter who really succeeded in using this method for quantitative work was Hamburger<sup>3</sup> who determined potassium as chloroplatinate. Since then, apparently no successful attempts to follow up this method for other purposes have been made, at least none have been found in the literature, until some years ago, however, the author succeeded in adapting Bülmann's method<sup>4</sup> for potassium determinations in this manner.

The present paper shows that the centrifugal method may also be used for determining calcium and magnesium, and phosphoric, sulfuric and nitric acids. Satisfactory results in all these cases have been obtained, as will be seen. Possibly the method could also be used for other precipitates heavier than water. The details of procedure are as follows. The precipitate obtained in the usual way is shaken with the mother solution and then transferred to tubes 2.5 cm. in diameter at the top and provided with a steep funnel below leading to a capillary tube about 4 cm. long (and for compact precipitates only 1 mm. in bore).<sup>5</sup> The precipitate is allowed to settle and by means of gentle shaking is, for the most part, caused to settle in the capillary stem. Many of these tubes are then centrifuged together until the precipitate in each has attained a constant height (which is usually the case in less than half an hour). The column is read with a mirror scale in order to avoid parallax in reading. These columns are reduced to the weight standard by comparison with a precipitate similarly obtained from a known weight of the substance similarly treated.

The following tables give results with different salts. In every table the first line shows the amount of the ion added expressed in milligrams. In the second line is given, for each case, the relative column height, and in the third line, that calculated under the assumption of direct proportionality. The reading limit mentioned at the right indicates the smallest amount of precipitate one is able to observe, assuming ability to read to within 0.1 mm. The agreement between the calculated and observed values is obviously very close. The results with nitric acid are especially interesting. The precipitate obtained with Busch's<sup>6</sup> nitron is bulky and flocculent; wide tubes had to be used and the usual

<sup>3</sup> Hamburger, see Ch. W. Purdy, "Practical Urine Analysis," 1895.

<sup>4</sup> Bülmann, *Medd. vetenskapsakad. Nobelinst.*, 1920.

<sup>5</sup> The tubes were calibrated by weighing with mercury.

<sup>6</sup> Busch, *Ber.*, 38, 861 (1905).

preparation tubes were taken. Nevertheless, in spite of the rather rough instruments, the results are exceedingly good. Of course one must make sure in all cases that the tubes compared have identical diameters.

SULFATE							Reading limit
H <sub>2</sub> SO <sub>4</sub> precipitated with BaCl <sub>2</sub>							
SO <sub>4</sub> , mg.	15	7.5	3.75	1.65	0.98	0.33	0.04
Vol. obs.	14.8	7.4	3.8	1.7	1.0	0.3	
Vol. calc.	15	7.5	3.8	1.7	1.0	0.3	

NITRATE										
$\text{HNO}_3$ precipitated with nitron										
$\text{NO}_3$ , mg.	8	4	4	2.64	2	1.3	1.2	0.8	0.4	0.03
Vol. obs.	10	5	5	3	2.5	1.5	1.5	1	0.7	
Vol. calc.	10	5	5	3.2	2.5	1.6	1.5	1	0.5	

CALCIUM							
Ca(OH) <sub>2</sub> acidified and precipitated as oxalate							
Ca, mg.	1.36	0.68	0.27	0.27	0.14	0.07	0.0045
Vol. obs.	16.0	8.0	3.2	3.2	1.6	0.8	
Vol. calc.	16.0	8.0	3.2	3.2	1.7	0.8	

ORTHOPHOSPHATE							
Na <sub>2</sub> HPO <sub>4</sub> precipitated with ammonium molybdate							
PO <sub>4</sub> , mg.	0.23	0.12	0.6	0.3	0.15		0.006
Vol. obs.	21.7	11.0	5.5	2.6	1.2		
Vol. calc.	22.0	11.0	5.5	2.7	1.3		

MAGNESIUM							
MgCl <sub>2</sub> precipitated with NaNH <sub>4</sub> HPO <sub>4</sub>							
Mg, mg.	3.85	2.31	1.54	0.38	0.19	0.09	0.007
Vol. obs.	20.5	11.9	8.0	1.8	0.9	0.5	
Vol. calc.	20.0	12.0	8.0	2.0	1.0	0.5	

A more complete study of this problem, involving a larger number of precipitates, should be of great advantage for analytical chemistry, for the method is both time-saving and simple.

The experiments have been carried out in the Wolcott Gibbs Memorial Laboratory at Harvard University and for his great kindness and good suggestions, I take this opportunity to express my warmest and heartiest thanks to the director, Professor Theodore W. Richards.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA.]

## TITRATIONS IN ETHYL ALCOHOL AS SOLVENT.

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The use of alcohol as a solvent in acid-base titrations may be advantageous for two reasons. The first is its solvent power for certain substances, such as the fatty acids, which are not soluble in water. The second is the somewhat greater sharpness of the end-points obtainable.<sup>2</sup> This is due to the fact that the dissociation of alcohol is much less than that of water<sup>3</sup> so that there is a greater range of hydrogen-ion concentration between an acid and an alkaline solution. For the same reason the degree of alcoholysis of salts of weak acids and bases is less than the degree of hydrolysis, so that the change in hydrogen-ion concentration through the end-point is more rapid in alcohol than in water. The alkalies in the alcohol system are the ethylates, so that the neutralization of a weak acid by sodium ethylate would be represented in the ionic form by the equation,  $HA + C_2H_5O^- = A^- + C_2H_5OH$ . While the dissociation of the acid, HA, is doubtless smaller in alcohol than in water, the dissociation of the alcohol is so much less than that of water as to account for the small degree of alcoholysis just mentioned. The alcoholysis of the salt is, of course, represented by the reverse equation.

For the titration of weak acids and bases it is necessary to select an indicator which changes color at the hydrogen-ion concentration existing at the true end-point, when the acid and base are present in equivalent quantities.<sup>4</sup> The purpose of this investigation has been to prepare an indicator scale for alcoholic solutions similar to those in common use for aqueous solutions.<sup>5</sup>

**Apparatus and Procedure.**—The hydrogen-ion concentration was measured by means of a hydrogen electrode<sup>6</sup> against a standard mercurous bromide electrode. The hydrogen electrode, instead of being of the foil type previously described by one of us, was a gauze cylinder similar to that originally used by Cottrell in this laboratory.<sup>7</sup>

<sup>1</sup> The preliminary work of this investigation was described in 1919 in the Master's Thesis by Esther B. Kittredge. The major portion of the data herein presented is taken from the Master's Thesis by Edna R. Bishop, 1921.

<sup>2</sup> Folin and Flanders, *THIS JOURNAL*, **34**, 774 (1912).

<sup>3</sup> An accurate determination of this constant is being made in this laboratory, and will shortly be published.

<sup>4</sup> Hildebrand, *THIS JOURNAL*, **35**, 847 (1913).

<sup>5</sup> E. g., Salm, *Z. physik. Chem.*, **57**, 471 (1907).

<sup>6</sup> The hydrogen electrode has been used previously, in alcoholic solutions by Hardman and Lapworth, *J. Chem. Soc.*, **99**, 2242 (1911); **101**, 2249 (1912); to determine the transport number of HCl and the effect of water upon it.

<sup>7</sup> Schmidt and Finger, *J. Phys. Chem.*, **12**, 406 (1908).

The standard electrode was made as described by Lewis, Brighton and Sebastian<sup>3</sup> substituting as electrode materials mercury, mercurous bromide and sodium bromide, 0.1 *N* in alcohol. Sodium bromide was substituted for the usual potassium chloride in order to get a more concentrated and hence better conducting electrolyte. The mercury used had been washed with nitric acid and distilled. The mercurous bromide was precipitated from c. p. sodium bromide and mercurous nitrate in the presence of mercury. It was then thoroughly washed with alcohol and 0.1 *N* sodium bromide in alcohol. The sodium bromide electrodes were reproducible within the limits of accuracy of the galvanometer.

The titrations were performed in a cell consisting of a beaker provided with a tight stopper through which were thrust the hydrogen electrode, the tip of the buret, an exit tube for hydrogen provided with a mercury seal, and the tube connecting with the standard electrode. The temperature was controlled to  $25 \pm 1^\circ$  by means of a hand-regulated thermostat. The rest of the apparatus was set up as described in previous papers from this laboratory.

The electromotive force of such a combination at  $25^\circ$  is given approximately by the familiar equation

$$E = E_0 - 0.059 \log c$$

where *c* is the hydrogen-ion concentration and  $E_0$  the electromotive force of the mercurous bromide electrode against a normal hydrogen electrode. The value of  $E_0$  has not yet been determined so that values will be given in terms of electromotive force instead of hydrogen-ion concentration.

If to an acid solution in the cell, sodium ethylate solution be added from the buret, and the e.m.f. plotted against the cubic centimeters of sodium ethylate added, a curve will be obtained in which the point of inflection represents the end-point of the titration. The shape of the curve will depend on the strength of the acid used.

The proper indicator for a given titration is one which changes color near the point of inflection of the e.m.f. curve. However, in order to determine where a given indicator changes color, an acid-base curve should be selected which is as flat as possible in the region of the color change, so that the e.m.f. may easily be controlled within narrow limits. It is necessary, therefore, to find acids and bases of various strengths so that the entire range from acid to base may be covered by flat portions of curves.

**Materials Used.**—It was found necessary to use chemicals free from oxidizing agents, in order that there should be no other reaction taking place at the electrode and that the e.m.f. obtained should be a true measure of the hydrogen-ion concentration. The alcohol was purified by distilling from conc. sulfuric acid (10–15 cc. of acid per liter of alcohol) to remove the amines and most of the water, distilling from silver nitrate

<sup>3</sup> Lewis, Brighton and Sebastian, *THIS JOURNAL*, 39, 2245 (1917).

(5 g. per liter) and a small amount of potassium hydroxide to remove the aldehydes and similar oxidizing bodies, and finally removing the last trace of water by shaking with calcium oxide for 2 days and distilling.

Sodium ethylate was prepared by dissolving metallic sodium in alcohol cooled in an ice-bath (at 0°). When the alcohol is not kept cold during the reaction resinous bodies are formed which seriously interfere with the constancy of the hydrogen electrode. As a simple means of obtaining the desired amount of sodium, it was sucked up while molten into glass tubes so that any desired length could be measured off and dissolved. The concentration of the solution could thus be determined by weighing the tubes before and after dissolving the sodium or by titrating with a standard acid solution.

The phenol was purified by distillation and kept in the dark, as the colored variety seemed to contain an oxidizing substance which affected the electrode.

Hydrochloric acid solution was prepared by dropping conc. sulfuric acid on sodium chloride, and passing the gas through calcium chloride into alcohol. Ammonium ethylate solution was prepared by dropping water on sodium hydroxide and ammonium chloride and passing the gas through soda lime into alcohol.

Aniline was purified as described by Gattermann,<sup>9</sup> omitting the ether extraction.

**Titration Curves.**—Fig. 1 gives titration curves of various acids with sodium ethylate and of bases with hydrochloric acid. Table I gives data concerning concentrations and end-points.

TABLE I			
Substance titrated (15 cc. of solution)	N	Titration solution	End-point Cc.
Acetic acid	0.068	NaOEt	14.2
Ammonia	0.2	HCl	9.2
Aniline	0.2	HCl	15.5
Chlorophenol	0.068	NaOEt	11.0
Maleic acid	0.0515	NaOEt	18.0
Palmitic acid	0.074	NaOEt	11.2
Phenol	0.2	NaOEt	8.5
Sulfuric acid	0.074	NaOEt	12.7

It required about 45 minutes for the solutions to become saturated with hydrogen and the electrode to come to equilibrium. After additions of

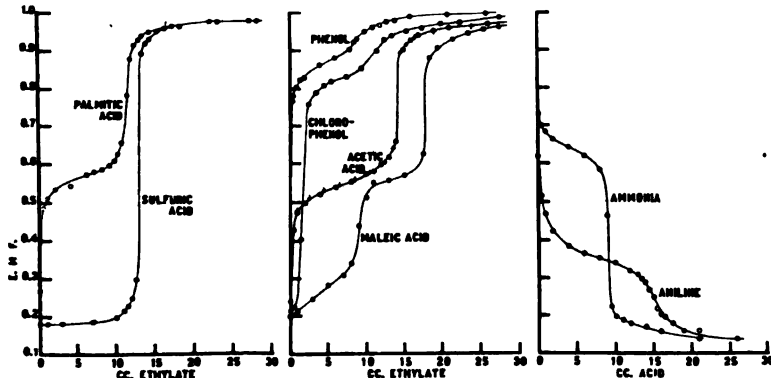


Fig. 1.—Titrations in ethyl alcohol solutions.

<sup>9</sup> Gattermann, "Practical Methods of Organic Chemistry," Macmillan and Co., 1903, p. 189.

titrating solution equilibrium was attained in about 10 minutes. The titrations are therefore much slower than when aqueous solutions are used.

It will be seen that the curves, as was expected, are very similar to those obtained for aqueous solutions, but that the difference in e.m.f. between acid and alkaline solutions is greater on account of the smaller dissociation constant of alcohol, as previously explained. The curves are quite reproducible, as illustrated by the two sets of points upon the curve for acetic acid.

**Table of Indicators.**—Examination of the curves obtained shows that the aniline and hydrochloric acid curve is flat enough for the determination

TABLE II  
COLOR CHANGES OF INDICATORS IN ETHYL ALCOHOL

Indicator	Conc. G. per l	No. of drops	Titration solution	E.m.f. of color changes
Bitter almond oil green	1.5	5	HAc-NaOEt	Green 0.69 colorless
Bromophenol blue	1	5	HCl-aniline	Yellow 0.34 green 0.47 blue
Cresol red	1	5	HCl-aniline	Pink 0.20, orange 0.30
Curcumin	Sat.	2	HAc-NaOEt	Greenish-yellow 0.66 red 0.85 orange 0.91 golden
Cyanine	1	8	HCl-aniline	Colorless 0.24 blue
Gallein	1	5	HAc-NaOEt	Rose 0.68 violet-blue
Iodeosin	Sat.	5	HCl-aniline	Golden-brown 0.20 pink
Methyl green	Sat.	8	HAc-NaOEt	Blue 0.66 lavender
Methyl orange	1	5	HCl-aniline	Pink 0.20 orange 0.23 yellow
Methyl violet	1	5	HAc-NaOEt	Violet 0.95 colorless
Methyl red	Sat.	9	HAc-NaOEt	Red 0.54 orange 0.62 yellow
Naphtholbenzoin	1	10	HAc-NaOEt	Light brown 0.70 blue
<i>p</i> -Nitrophenol	1	5	HAc-NaOEt	Colorless 0.61 yellow-green
Phenolphthalein	10	5	Phenol-NaOEt	Colorless 0.68 red
Resorcin blue	1	5	HAc-NaOEt	Red 0.39 blue
Rosalic acid	1	5	HAc-NaOEt	Golden 0.58 orange 0.65 pink
Sodium alizarin sulfo- nate	Sat.	10	HAc-NaOEt	Greenish - yellow 0.50 orange 0.57 rose 0.82 violet
Thymol blue	1	10	HCl-aniline	Red 0.30 golden
Thymolphthalein	10	5	Phenol-NaOEt	Colorless 0.82 blue
Trinitrobenzene	Sat.	5	HAc-NaOEt	Colorless 0.68 golden-orange
Tropaeolin	Sat.	5	HCl-aniline	Salmon-pink 0.20 orange 0.23 golden
Tropaeolin OO	Sat.	5	HCl-aniline	Pink 0.15 orange 0.20 yellow

of the color changes of indicators from about 0.14 to 0.45 volts, acetic acid and sodium ethylate from 0.45 to 0.70 volts and from 0.90 to 0.97 volts, *p*-chlorophenol and sodium ethylate from 0.75 to 0.98 volts. These three pairs practically cover the range.

After the titration curves were obtained it was unnecessary to repeat the titration with the hydrogen electrode with each indicator investigated. Time was saved in most instances by determining the amounts of acid and base required to produce a certain color change and then finding the corresponding e.m.f. from the original hydrogen-electrode curve. This indirect method was indeed necessary with such indicators as trinitrobenzene which oxidized the hydrogen electrode, thus giving values for the e.m.f. which were not true measures of the hydrogen-ion concentration.

The indicators investigated, concentration, number of drops used and e.m.f. of the color change are given in Table II. The positions of most of the indicators in alcohol are close to their positions in water but there are exceptions, *e. g.*, cyanine is considerably displaced toward the acid side, and some indicators which are useful in water cannot be used at all in alcohol. The e.m.f.'s of the color changes are accurate to approximately 0.03 volts. Of course the color does not change abruptly at the e.m.f. given, so that the figures should be considered as indicating a color intermediate between the two limiting colors.

**Titration of Fatty Acid in Presence of Fat.**—As an illustration of the use of the indicator table we will give results for the titration of a free fatty acid in the presence of its glyceride, a problem of some analytical importance. Palmitic acid and palmitin were selected for the purpose. By reference to Fig. 1, it will be seen that palmitic acid is neutralized by sodium ethylate at about 0.8 volt so that thymolphthalein should change color close to the true end-point. The following table gives the results of four titrations with 0.157 *N* sodium ethylate solution, tripalmitin being present in each case nearly to the point of saturation.

TABLE III

Solvent alcohol	Palmitic acid	
	Taken G.	Found G.
Absolute.....	0.467	0.467
Absolute.....	0.493	0.490
Commercial 95%.....	0.513	0.512
Commercial 95%.....	0.436	0.439

The results show that an accurate titration is possible by this means, and further that extreme dehydration of the alcohol is unnecessary. The chief effect of small amounts of water is to decrease the solubility of the fat and thus retard the titration.

It is obvious that suitable indicators can be selected by the aid of Table II for the other titrations represented by the curves in Fig. 1. For example,



the end-point for ammonia corresponds to about 0.38 volt, but the curve is steep between 0.25 volt and 0.53 volt. Evidently, therefore, bromophenol blue, changing at 0.34 volt, or resorcin blue, changing at 0.39 volt, should give a sharp end-point in the titration of ammonia.

### Summary.

Hydrogen-electrode titration-curves are given for a number of reactions in the ethyl alcohol system, together with a table of indicators for use in such reactions. The possible applications of the data obtained are illustrated by the titration of a fatty acid in the presence of its glyceride.

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### NOTE.

**The Relation Between Entropy and Probability.<sup>1</sup> The Integration of the Entropy Equation.**—The rate of increase of the specific heat with the entropy of a given element or compound depends upon the probability of the randomness of the individual particles. At the absolute zero, or at the point of zero kinetic energy we are quite certain that each particle will remain in a fixed position. The probability, therefore, will be unity. At relatively high temperatures the probability of that state prevailing is very nearly zero. Now, the mathematical expression of the above statements may be assumed to be proportional to the term,  $\frac{C_{\infty} - C}{C_{\infty}}$ ,

which at the absolute zero is unity and at relatively high temperatures approaches zero, or,

$$\frac{dC}{dS} = K \left\{ \frac{C_{\infty} - C}{C_{\infty}} \right\} \quad (1)$$

Assuming that when  $C$  is zero  $S$  is also zero, Equation 1 on integration gives,

$$S = \frac{C_{\infty}}{K} \log \frac{C_{\infty}}{C_{\infty} - C} \quad (2)$$

The value of  $K$  may be readily obtained by substituting in Equation 1  $CdT/T$  for its equal  $dS$  and integrating. Thus,

$$\frac{dC}{dT} = \frac{K(C_{\infty} - C)C}{C_{\infty} T} \quad (3)$$

<sup>1</sup> The specific heats of all solid substances decrease with the temperature and approach zero as the absolute temperature approaches zero. This experimental fact led to the assumption that at the absolute zero of temperature the specific heat of all substances is actually zero. Following this announcement many attempts were made, notably by Einstein, (*Ann. Physik*, [4] 22, 180 (1907)), Nernst and Lindemann, (*Sitzb. Akad. Wiss. Berlin.*, 494, 1911), Debye, (*Ann. Physik*, [4] 39, 789 (1912)), and by Planck, "Theorie der Wärmestrahlung," to express the specific heat as a simple function of the absolute temperature, but with no success.

Whence,

$$\log \frac{C}{C_{\infty} - C} = K \log T + \log k \quad (4)$$

In the straight line equation (4)  $K$  is the slope, and  $\log k$  is the intercept on the ordinate.<sup>2</sup> This equation may of course be written in the simpler form,

$$C = \frac{C_{\infty} k T^K}{k T^K + 1} \quad (5)$$

Equation 4 or 5 reproduces the experimental data, within the probable error, for the specific heats of all substances thus far obtained by thermo-electric methods.

The following table giving the results for copper demonstrates this.

TABLE I  
CALCULATIONS OF THE SPECIFIC HEAT OF COPPER AT DIFFERENT TEMPERATURES BY  
THE FORMULA  $C = \frac{C_{\infty} k T^K}{k T^K + 1}$

1 $T$	2 $C_p$ (obs.)	3 $C_p$ Calc.	4 Diff.	1 $T$	2 $C_p$ (obs.)	3 $C_p$ Calc.	4 Diff.
Dutch (Leyden Laboratory)				English			
14.51	0.04	0.04	0.00	50.00	1.32	1.28	+0.04
15.59	0.05	0.05	0.00	90.00	3.98	3.57	+0.41
17.17	0.07	0.07	0.00	130.00	4.78	4.84	-0.06
20.19	0.11	0.11	0.00	170.00	5.23	5.39	-0.16
20.74	0.12	0.12	0.00	210.00	5.50	5.64	-0.14
25.37	0.23	0.22	+0.01	250.00	5.70	5.77	-0.07
29.73	0.38	0.34	+0.04	290.00	5.83	5.83	0.00
40.22	0.83	0.75	+0.08	390.00	6.09	....	.....
50.04	1.43	1.28	+0.15	German (Nernst Laboratory)			
59.75	2.06	1.86	+0.20	23.5	0.22	0.18	+0.04
60.33	2.08	1.90	+0.18	27.7	0.32	0.28	+0.04
69.66	2.59	2.47	+0.12	33.4	0.54	0.46	+0.04
80.32	3.05	3.08	-0.05	87.0	3.33	3.43	-0.10
88.86	3.37	3.50	-0.13	88.0	3.38	3.47	-0.09
89.39	3.44	3.55	-0.11	137.0	4.57	4.98	-0.41
				234.0	5.59	5.72	-0.13
				290.0	5.79	5.83	-0.04
				323.0	5.90	5.87	+0.03

$$C_{\infty} = 3 \quad R = 5.966$$

$$\log k = -5.4955$$

$$K = 2.900$$

The figures of Cols. 1 and 2 were collected by Dr. Latimer, Gilman Hall, University of California.

In the table following are given in the second and third columns, the values for  $K$  and for  $K_1$ , or  $\log k$ , obtained from the straight line experimental plots according to Equation 4; in the fourth column are given the

<sup>2</sup> Actually, the raw experimental  $C_p$  values were used in the straight line plots, as the increase in volume is negligibly small up to 100° A. and in some cases even up to 200° A.

specific heats per gram atom for constant volume, calculated from the values of  $K$  and  $K_1$  with the aid of Equation 4 or 5. In the fifth column are given the entropies per gram atom or mol, calculated by means of Equation 2, and in the sixth column are given the values for the entropies obtained by Lewis and Gibson<sup>3</sup> by a graphical method.

Since Lewis and Gibson state that their calculated values are accurate to from 0.3 to 2.0 units of entropy the agreement between the two columns is entirely satisfactory. However, the values obtained by means of Equation 2 are slightly but consistently higher in most cases. This is due to the fact that for very low temperatures for which there are no available data Lewis and Gibson join to their graphical method the equation,

$$C = aT^3, \text{ whence } S = \frac{1}{3} C.$$

This is equivalent to the assumption that in Equation 1  $(C \propto -C)/C \propto$  remains unity at very low temperature and that  $K=3$  which is evidently not true, as a glance at the table will show.

TABLE II  
ENTROPIES AT CONSTANT VOLUME

	$K$	$K_1$	$C_p$ (298)	$S_p$ (298) Calc. (Eq. 2)	$S_p$ (298) Lewis & Gibson
Al.....	2.90	-5.6985	5.774	7.07	6.7
Cu.....	2.90	-5.4955	5.844	8.00	7.8
C, diamond.....	2.80	-7.4088	1.482	0.61	0.6
C, graphite.....	1.83	-4.7946	2.093	1.41	1.3
KCl.....	2.47	-4.3320	5.870	19.90	19.4
NaCl.....	2.94	-5.4008	5.887	17.55	17.2
PdCl <sub>2</sub> .....	1.88	-3.1133	5.798	33.99	33.2
Na.....	2.334	-3.7157	5.916	12.23	11.7
I.....	1.84	-2.5074	5.911	15.20	14.8
Pb.....	2.18	-2.9652	5.943	15.21	15.0
S, rhombic.....	1.23	-2.4418	4.771	7.80	7.4
S, monocl. ....	1.30	-2.5627	4.882	7.83	7.6
Sn, gray.....	2.24	-4.0162	5.794	9.23	....
Sn, white.....	2.79	-4.7626	5.922	10.50	....
Cd.....	6.00	-10.2960	5.965	8.65	....
Ca.....	2.53	-4.3570	5.892	10.35	10.3
HgCl.....	1.60	-2.6235	5.702	23.26	23.2
Zn.....	2.40	-4.2204	5.880	10.54	9.7
Ag.....	2.36	-4.0875	5.862	10.24	9.9
Mg.....	2.57	-4.8409	5.790	8.18	8.1
CO(NH <sub>2</sub> ) <sub>2</sub> .....	0.705	-1.7485	2.969	46.62	41.0

$\pm 2^\circ$

\* This value is taken from a paper by Gibson, Latimer and Parks, (THIS JOURNAL, 42, 1541 (1920)). On plotting the values of  $C_p$ , calculated by means of Equation 5, and also the experimental values for  $C_p$  against  $\log T$ , the difference was found to be  $8(0.035)$ , whence  $S_p(298) = 46.9$ .

EUREKA, CALIFORNIA.  
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GEORGE A. LINHART.

<sup>3</sup> Lewis and Gibson, THIS JOURNAL, 39, 2554 (1917), Tables VI, VIII.

**The Formation of Potassium Perchlorate from Potassium Chlorate.—**

The action of certain of the stronger acids on potassium chlorate is not commonly considered as a method applicable to the preparation, in the laboratory, of potassium perchlorate. The action of sulfuric acid on potassium chlorate with the formation of the perchlorate was first recorded by Stadion.<sup>1</sup> Later, Penny<sup>2</sup> noted that nitric acid acting on the chlorates of potash and soda yielded perchlorate; and shortly after, Millon<sup>3</sup> speaks of the formation of the perchlorate by the action of sulfuric acid on the chlorate.

While the action of strong sulfuric acid on potassium chlorate, yields as it does at first, perchlorate and the oxides of chlorine, consisting largely of the tetroxide, the explosive character of the reaction is such that it is very difficult to control. It can, however, be carried out without danger by adding the sulfuric acid slowly and avoiding warming. Decomposition is complete in about 5 hours and is shown by the disappearance of the yellow color accompanying the decomposition of the chlorate. When 2 to 5 g. of chlorate is treated with 50 cc. of conc. sulfuric acid, the yield of perchlorate is about 11%.

Nitric acid of various degrees of concentration will convert potassium chlorate to the perchlorate. A good procedure consists in repeated evaporations to dryness of the chlorate on the steam-bath with ordinary conc. nitric acid. The final product is only the nitrate and perchlorate the yield being as high as 30%. Anhydrous nitric acid gives with potassium chlorate just about the same amount of the perchlorate when evaporated on the steam-bath as does ordinary concentrated acid. Fuming nitric acid, doubtless on account of the reducing character of the acids of nitrogen contained, yields almost no perchlorate.

Phosphoric acid with chlorate yields perchlorate. When the chlorate is boiled with 85% phosphoric acid until the disappearance of the yellow chlorine color, a yield of as high as 15% of perchlorate is obtained.

Chromium trioxide and chlorate, boiled with just enough water to keep the mixture in solution, afford a yield of about 11% of perchlorate.

When chloric acid in a concentration of 30% is allowed to stand for several days in contact with potassium chlorate, then warmed and evaporated with hydrochloric acid in order to destroy all chloric acid and chlorate, no perchlorate is obtained.

Certain acids do not decompose the chlorate, even at the boiling temperature. Among these may be mentioned saturated oxalic acid solution, 25% tartaric acid, acetic acid both glacial and dilute, 50% monochloro-acetic, 25% lactic, 50% arsenic, 20% permanganic and persulfuric acid. Other acids, such as formic, trichloro-acetic, hydrofluoric, and hydrochloric acids decompose the chlorate but without yielding perchlorate.

<sup>1</sup> Stadion, *Gilbert's Ann.*, 52, 197 (1818).

<sup>2</sup> Penny, *Brit. Assoc. Rep.*, 1840, 79.

<sup>3</sup> Millon, *Ann. Chem.*, [3] 7, (1843).

Reference to the hydrogen-ion concentration of these various acids gives no apparent reason for the behavior of the various acids. A view to be considered is that the action is selective and follows along the same lines as that of heating the chlorate alone, when rearrangement takes place, 3 molecules of the chlorate being oxidized at the expense of another molecule. In the cases of the action of certain acids on the chlorate, we have the same general character of reaction going on, only at lower temperatures than when the chlorate is heated alone.

MADISON, WISCONSIN.

Received October 8, 1921.

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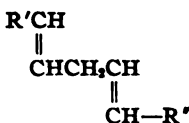
[CONTRIBUTION FROM THE KENT CHEMICAL LABORATORY OF THE UNIVERSITY OF CHICAGO.]

### **C<sub>18</sub> ACIDS. III. FOUR TETRAHYDROXY-STEARIC ACIDS DERIVED FROM LINOLIC ACID, AND THEIR SIGNIFICANCE WITH REGARD TO THE LINOLIC ACID OF COMMON OILS.**

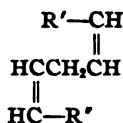
BY BEN H. NICOLET AND HENRY L. COX.<sup>1</sup>

Received August 4, 1921.

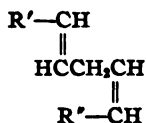
In spite of the relatively considerable amount of work that has been done on linolic acid, C<sub>18</sub>H<sub>32</sub>O<sub>2</sub>, our knowledge of its chemistry is rather strikingly limited. There is a moderate amount of evidence<sup>2</sup> that its formula is represented by (I) CH<sub>3</sub>(CH<sub>2</sub>)<sub>4</sub>CH=CHCH<sub>2</sub>CH=CH(CH<sub>2</sub>)<sub>7</sub>CO<sub>2</sub>H. Four space isomers of such a substance are possible.



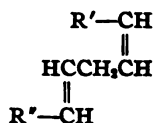
(II).  
trans-trans



(III).  
cis-cis



(IV).  
cis-trans



(V).  
trans-cis

in which R' represents the radical CH<sub>3</sub>(CH<sub>2</sub>)<sub>4</sub>— and R'' represents (CH<sub>2</sub>)<sub>7</sub>CO<sub>2</sub>H. No attention has apparently been paid to the question of which, or how many of these occur in natural glycerides, except for Bedford's<sup>3</sup> suggestion that there are two different acids of this formula, because the addition of bromine yielded two tetrabromides. Takahashi<sup>4</sup> has shown further that the α-tetrabromide (m. p. 114°) of linolic acid, when treated with zinc under proper conditions for the elimination of bromine, gives a linolic acid which, on re-bromination, yields two or more tetrabromides (two crystalline products, and an oil which may or may not have been a mixture of these). Each of these products, on removal of bromine, re-

<sup>1</sup> The material here presented is used by Henry L. Cox in partial fulfilment of the requirements for the degree of Doctor of Philosophy in the University of Chicago.

<sup>2</sup> Goldsobel, *Chem. Ztg.*, 1906, 825.

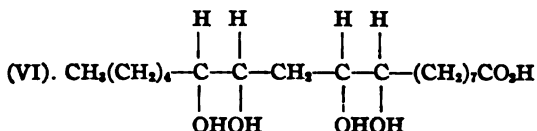
<sup>3</sup> Bedford, *Dissertation*, Halle a. S., 1908.

<sup>4</sup> Takahashi, *J. Tokyo Chem. Soc.*, 40, 233-89 (1919); *C. A.*, 13, 1583 (1919).

generates a "linolic acid" which, when again brominated, yields the same three products as before, and in approximately the same proportions, whichever tetrabromide served as a starting point. The elimination, and perhaps also the re-addition, of bromine occurs in more than one way.

Again, the oxidation of linolic acid with alkaline permanganate gives at least two (the published data might suggest a larger number)<sup>6</sup> tetrahydroxy-stearic (sativic) acids. This list of things unknown need not be further extended to indicate the need for further information concerning linolic acid.

Since sativic acid (VI) contains 4 asymmetric carbon atoms, it is ob-



vious that 16 optically active forms are possible, or 8 inactive forms (*dl*-mixtures or racemates). As has been suggested, 2 of these 8 are probably known, as products of permanganate oxidation.

It has been shown that, at least for the stereo-isomeric oleic and elaidic acids, addition takes place in only one way in the course of oxidation with permanganate. Thus oleic acid yields only a dihydroxy acid, m. p. 132–3°, while elaidic acid yields only an isomer, m. p. 99–100°. Albitzky<sup>6</sup> has described a method by which addition seems to occur only in the reverse direction. This consists in the addition of hypochlorous acid to the double bond, with subsequent replacement of the chlorine by hydroxyl, by means of caustic alkali. By this method, Albitzky obtained from oleic acid a dihydroxy-stearic acid corresponding to the product obtained from elaidic acid with potassium permanganate. Similarly treated, elaidic acid gave the dihydroxy acid obtained from oleic acid by direct oxidation.

If it be assumed that linolic acid will behave, with reference to permanganate and hypochlorous acid, as Albitzky showed oleic acid to act with these reagents, it follows that a study of the sativic acids obtained by these different methods, can throw some light on the space structures of the original linolic acids. This has been found to be the case.<sup>7</sup>

The oxidation of linolic acid with permanganate produces 2 different sativic acids,<sup>8</sup> m. p. 170° and 153°, respectively. The existence of 2

<sup>6</sup> Cf. Lewkowitsch, "Chemical Technology of Oils, Fats and Waxes," 5th Ed., 1913, vol. I, pp. 232–3, for list of references.

<sup>7</sup> Albitzky, *J. prakt. Chem.*, [2] 61, 65 (1900).

<sup>8</sup> Strictly speaking the results and conclusions here reported, apply to linolic acid regenerated from the tetrabromide, m. p. 114°. But the natural linolic acid gives, so far as reported, such similar results on bromination and oxidation, that the acid of ordinary oils may be at least suspected of being identical with the regenerated acid.

<sup>9</sup> Meyer and Beer (*Monatsh.*, 33, 325 (1912)) oxidized the fatty acids of the seed oil of "Jimson weed" (*Datura stramonium*) and obtained an "α-sativic acid," m. p.

sativic acids, as indicated by various previous observers,<sup>8</sup> is thus confirmed by the work here reported, in which for the first time both acids are isolated from a single oxidation experiment. The fact that 2, and essentially only 2, sativic acids were isolated (although a relatively much smaller quantity of lower melting material, which may perhaps be an isomeric sativic acid, was obtained) points to the fact that 2 stereo-isomers of linolic acid were present originally. It is conceivable, though not in accord with the behavior of oleic acid on oxidation, that both of these acids might come from a single linolic acid; but this would not account for the additional sativic acids later described.

The addition of hypochlorous and hypobromous acids to linolic acid<sup>9</sup> was found to take place smoothly, and a method was developed which permitted the transformation of these substances to sativic acids, though the yields, never over 14%, left much to be desired. The first step in this transformation, the formation of tetra-acetyl-sativic acid, was accomplished with a yield of 85%. Hydrolysis of the tetra-acetate, however, gave a large amount of by-products, probably due to a splitting off of acetic acid from the partially hydrolyzed molecule to give ring compounds containing oxygen.<sup>10</sup>

Two new sativic acids, m. p. 144.5° ( $\gamma$ -acid), and 135° ( $\delta$ -acid), were thus obtained, differing in melting point and solubility from those obtained by direct oxidation. No indications of the formation of  $\alpha$ - or  $\beta$ -acid were obtained in this product.

Since only 2 sativic acids were obtained by the permanganate oxidation of linolic acid, while 2 and only 2 additional sativic acids were obtained from the hypobromous acid addition product, it is concluded that 2 and essentially only 2 of the possible stereo-isomeric forms (II-V) are present in "ordinary" linolic acid. This limits the possibilities to six combinations, as follows:

A, II and III  
B, II and IV

C, II and V  
D, III and IV

E, III and V  
F, IV and V

Further, as *cis* (or *trans*) addition yields  $\alpha$ - and  $\beta$ -sativic acids, while *trans* (or *cis*) addition yields the  $\gamma$ - and  $\delta$ -acids, it is not unreasonable to eliminate 2 of these pairs, A and F. Examination of the space formulas will show that *trans* addition at the double bonds of (II) or (V) will give 163°, and a " $\beta$ -sativic acid," m. p. 173°. As the same oil yielded a tetrabromo-stearic acid, m. p. 117°, whereas the highest recorded melting point of linolic acid tetrabromide is 114°, it is not certain that these were true linolic acid derivatives. However, in conformity with their system, the acid of higher melting point (170°) obtained in this work, will be called the  $\beta$ -acid, and the second, (m. p. 153°) the  $\alpha$ -acid.

<sup>9</sup> Albitzky, Ref. 6, has prepared the corresponding addition products of several acids of the oleic series.

<sup>10</sup> There is here the possibility of forming oxide rings containing from 3 to 6 atoms. The relative ease of formation and stability of 5- and 6-membered rings, is well known.

the same product as *cis* addition at the corresponding bonds of (III) and (V), and *vice versa*.

The evidence is thus fairly conclusive that there are 2 stereo-isomers present in ordinary linolic acid, and that choice of the 2 forms is limited to 4 possibilities, B, C, D, and E, above. A further limitation of choice cannot be definitely made in the present state of our knowledge of linolic acid and its derivatives; but it may be of interest to consider certain indirect evidence that makes possible a fairly plausible guess, for by making use of two not unreasonable assumptions the number of possibilities can be narrowed much further.

It has been shown that when bromine is added to oleic or elaidic acid, and subsequently removed with zinc, only the original acid is obtained. Linolic acid, however, behaves in a different manner.<sup>4</sup> Isomerization takes place in the latter case, but not in the former; but even linolic acid produces only 2 of the 4 possible isomers, so that even here but one double bond has been affected. The first assumption, then, is that the double bond in the 9, 10 position (common to oleic and linolic acids) is the one *not* affected. This excludes the 2 combinations B and E (above), on account of the different space arrangement of the 9-10 double bond in these pairs of isomers. The choice is thus limited to the 2 pairs, C and D.

It is the universally observed rule that the naturally occurring higher fatty acids of the oleic series are the *trans* forms.<sup>11</sup> The *cis* forms are known only as artificially prepared from these.

The second assumption, then, is that linolic acid, also, should have a *trans* structure with regard to its 9-10 double bond. Inspection of the formulas shows that only (II) and (V) fulfil this condition, and these are accordingly the linolic acids most probably present in the natural glycerides, and in linolic acid as prepared from them by the usual methods.

It should be understood that present evidence is not definitely sufficient to limit the choice of stereo-isomers further than to the 4 pairs above mentioned, without the introduction of assumptions that have at present no particularly firm experimental foundation. A certain amount of speculation is however justified by the fact that present synthetical methods do not make likely the synthesis in the near future of any homogeneous sativic acid, by methods which would indicate a really definite space-structure.

### Experimental Part.

**Preparation of Linolic Acid Tetrabromide.**—The starting material was the dried fatty acids of cottonseed oil. Of several methods tried, the following gave the best results. A slight excess of bromine (as shown by a faint permanent red color) was added gradually to a well-stirred solution of 200 g. of fatty acids in 1000 cc. of ligroin (b. p. 70–100°) cooled to 0°. The mixture was boiled, filtered hot, and allowed to crystal-

<sup>11</sup> Lewkowitsch, Ref. 5, pp. 178, 195, 213.



lize. After filtering and washing with ligroin of lower boiling point, 88 g. of tetrabromide, m. p.  $113^{\circ}$  without further purification, was obtained. More than a kilogram of tetrabromide was prepared by this method.

**Linolic Acid.**—This was prepared from the tetrabromide in the usual way, by refluxing it for 24 hours with zinc and 8% alcoholic hydrochloric acid, followed by saponification of the ester. The yields averaged 97%, and the purity, as judged by the iodine number, ranged from 86–99%.

**Dichloro-dihydroxy-stearic Acid.**—Linolic acid (11 g.) was dissolved in 500 cc. of 1% potassium hydroxide solution, and slightly more than 2 mols of 2 *N* potassium hypochlorite was added. (The sodium soaps are so slightly soluble that their use requires an almost prohibitive volume of solution.) A slow stream of carbon dioxide was then led through the solution. A white, gummy mass precipitated within a short time, but the gas was passed for several hours, or until a small sample of the solution, removed for testing, showed little or no test for hypochlorite. Excess of the latter was then destroyed with bisulfite and dil. sulfuric acid, and the solution extracted with ether. The light brown viscous oil obtained, would not crystallize, and could not be made to distil under 10 mm. pressure. The iodine number (2.3%) showed nearly complete reaction.

*Analysis* (Carius). Calc. for  $C_{18}H_{34}O_4Cl_2$ : 18.92. Found: Cl, 18.98.

All the products intermediate between linolic acid and  $\gamma$ - and  $\delta$ -sativic acids, showed themselves incapable of crystallization or of distillation. Their definite characterization, and preparation in a high state of purity, must therefore be left for future work.

**Dibromo-dihydroxy-stearic Acid.**—This was prepared in very much the same manner as was the chloro compound, but saturation with carbon dioxide was carried out at  $0^{\circ}$ , on account of the less stability of hypobromous acid. From 40 g. of linolic acid, 59 g. of a viscous brown oil was obtained.

*Analysis* (Carius). Calc. for  $C_{18}H_{34}O_4Br_2$ : 33.7 Found: Br, 31.3, 31.1.

Iodine number. Calc., 0.0. Found: 8.5.

The bromine determination thus indicates a purity of 93%, while the iodine absorption points to a 95% conversion of the linolic acid. It appears to be possible to prepare this acid with a purity of more than 90%, and in view of the character of the product, better results were scarcely to be expected.

**Tetrahydroxy-stearic Acid Tetra-acetate (Sativic Acid Tetra-acetate).**—When dichloro-dihydroxy-stearic acid was heated with sodium acetate and acetic anhydride for periods of 3 to 21 hours, the product contained much chlorine, and gave no sativic acid on saponification. The substitution of silver acetate for sodium acetate gave no better results. When potassium acetate was used, and the mixture refluxed 45 hours, an oil was obtained which gave the following analytical data.

Acid number. Calc.: 92.2. Found: 83.2, 88.8.

Saponification number. Calc.: 543. Found: 489.2.

Obviously, therefore, the product was rather impure, but consisted chiefly of sativic acid tetra-acetate. It still contained 2.3% of chlorine.

When dibromo-dihydroxy-stearic acid was refluxed with dry potassium acetate and acetic anhydride, the reaction was much more rapid. A precipitate of potassium bromide began to appear almost at once, and at the end of 5 hours, represented 74% of the bromine theoretically present. This method, with slightly longer heating, proved to be the best for preparing the tetra-acetyl derivative.

**Saponification of Sativic Acid Tetra-acetate.**—Sativic acid is somewhat soluble in hot water, and insoluble in ether. It was by these preliminary tests that the success of various methods of hydrolysis of its tetra-acetate was judged. Alcoholic sodium or

potassium hydroxide gave yields of sativic acid of 3-4%, regardless of whether the reaction was carried out at ordinary or higher temperatures. Sodium carbonate in aqueous-alcoholic solution gave about the same result. Hydrolysis with a 1% alcoholic solution of hydrochloric acid (Gattermann's method for saponification of ethylene di-acetate) gave less good results, although important amounts of ethyl acetate were formed. Dil. aqueous sulfuric acid was equally unsuccessful in giving the desired results.

The best yields of sativic acid were obtained by hydrolysis of the tetra-acetyl derivative with hot aqueous sodium hydroxide, for a period of one hour. The solution, diluted to 1 liter for each 10 g. of original substance, acidified, allowed to stand overnight, and washed with ether, gave 12-14% of sativic acid. Better yields could not be obtained. The exceptional opportunity for the formation of cyclic oxides in this case, has already been mentioned.

The ether-soluble portions of the residues from these hydrolyses were saved, and an attempt made to distil them. Under a pressure of less than 1 mm., distillation occurred only in part, and with obvious decomposition, above 300°.

**Sativic Acids Derived from Dihalogeno-dihydroxy-stearic Acids.**—As the product obtained directly from the hydrolysis of dichloro-dihydroxy-stearic acid was the same in melting point, 140-3°, and in all of its observed properties, as that from the bromine analog, the two were used interchangeably in the later work.

Preliminary attempts to purify the sativic acid obtained by hydrolysis of the tetra-acetyl derivative, indicated separation into 2 portions, m. p. 135° and 144° respectively. Accordingly, 3 g. of these sativic acids, previously recrystallized once from water was boiled for 15 minutes with 200 cc. of water, containing a few drops of hydrochloric acid, filtered hot, and this extraction process repeated as long as any residue remained. Flocculent precipitates were deposited as all the filtrates cooled. After filtration and washing with ether, the following 5 fractions were obtained.

Fraction	TABLE I	
	Wt. G.	M. p. °C.
1.	1.25	Below 120
2	0.45	135
3	0.25	135
4	0.22	144-5
5	0.05	145

Fractions 2 and 3 were combined and recrystallized from 50% acetic acid, then from 50% alcohol. As the melting point remained constant at 135°, the material was considered to be pure, and designated  $\delta$ -sativic acid. Similarly treated, Fraction 4 retained its melting point, 144.5°, and was designated  $\gamma$ -sativic acid. Analysis gave the following results.

	Analyses		
	$\gamma$ -Acid M. p. 144.5° %	$\delta$ -Acid M. p. 135° %	Calc. for C <sub>18</sub> H <sub>34</sub> O <sub>8</sub> %
Carbon.....	61.87 62.26	61.89 .....	62.03 .....
Hydrogen.....	10.42 10.50	10.21 .....	10.42 .....
	Solubility		
	G.	G.	
100 g. of boiling water dissolves.....	0.20	0.39	.....
	Equiv. wt.		
(By titration).....	351.5	.....	348.4

Although these two acids differ rather strikingly in melting point and in solubility, the melting point of the  $\delta$ -acid is not lowered by admixture of a small amount of the  $\gamma$ -acid. Accordingly, a series of mixtures was made containing known amounts of each acid, and the temperatures estimated at which melting began, and was complete. The results, plotted in Fig. 1, Curve 2, showed that mixtures melted over much wider ranges than the pure substances, and that the formation of solid solutions (rather common among the higher fatty acids) was indicated. All the evidence, therefore, indicates the formation of 2 different sativic acids in this series of reactions.

**Oxidation of Linolic Acid.**—The procedure adopted was that of A. Rollet,<sup>13</sup> essentially an oxidation with cold, dilute, alkaline permanganate. The product was dried and extracted with ether for 8 hours, the residue being a white powder which constituted a 54% yield of crude sativic acid. It melted at 162–8°, and recrystallization from alcohol had very little purifying effect. This was also the experience of Rollet; but his further results<sup>13</sup> were not in accordance with those here described. Treatment with benzol had no appreciable effect. The crude product was therefore treated with water, as in the case of the  $\gamma$ - and  $\delta$ -acids.

Twelve g. of ether-extracted sativic acid was boiled for several minutes with 2.5 liters of water containing 4 cc. of conc. hydrochloric acid. The solution was filtered hot, and the filtrate allowed to cool. The residue was boiled again with acidified water, and the process repeated as long as any material crystallized as the solution cooled. To prevent too great loss, the mother liquor from the first fraction was used as solvent for the third and fifth fractions, and that from the second, for the fourth and sixth. Six fractions were collected as shown.

TABLE II

Fraction	Wt. G.	M. p. °C.	Fraction	Wt. G.	M. p. °C.
1	2.30	148–150	4	0.85	170–171
2	1.95	153.5–4.5	5	0.95	169–170
3	1.50	165–169	6	0.45	169–171

Other samples were treated in the same way with similar results. The melting points indicate a partial separation into at least two substances.

The various fractions of several preparations were recombined to form three new fractions: A, all fractions melting from 145° to 150°; B, all fractions melting from 152° to 155°; C, all fractions melting from 170° to 172°.

Fraction A was fractionated into 14 portions by the procedure outlined above. All but the first and last two melted between 150° and 154°, and were combined and crystallized several times from glacial acetic acid and from alcohol. After the first time, the product melted constantly at 153°, and was considered to be pure  $\alpha$ -sativic acid. A further quantity of identical material was obtained by crystallizing fraction B from acetic acid.

When Fraction C was crystallized from acetic acid, the melting point, after the first time, remained constant at 170°. This material is evidently the sativic acid commonly described, and is here called the  $\beta$ -acid.

While it is fairly obvious from the data given that these two products are different and isomeric, the melting point of the  $\alpha$ -acid is not depressed by admixture with the other. Curve 1 (Fig. 1), which shows the temperatures at which melting begins, and at which it is complete, for mixtures of various compositions, indicates the formation of solid

<sup>13</sup> A. Rollet, *Z. physiol. Chem.*, 62, 410 (1909).

<sup>14</sup> A. Rollet, Ref. 12. "When, however, the substance (*i. e.*, crude sativic acid) was boiled with 50 parts of benzol, in which only a minimal trace dissolved, and was again crystallized from alcohol, the melting point was 171–3°."

Analyses			
	$\alpha$ -Acid M. p. 153° %	$\beta$ -Acid M. p. 170° %	Calc. for $C_{18}H_{34}O_8$ %
Carbon.....	61.66 61.96	62.14 62.11	62.03
Hydrogen.....	10.37 10.55	10.50 10.40	10.42
Solubility			
	G.	G.	
100 g. of boiling water dissolves...	0.10	0.04	
	Equiv. wt.		
(By titration).....	349.0	345.0	348.4

solutions. At the same time, it adds one more proof that the two acids are different.

The  $\beta$ -acid corresponds closely to the sativic acid obtained by Hazura,<sup>14</sup> Rollet<sup>15</sup> and others. With the possible exception of Meyer and Beer<sup>8</sup> no previous investigators have mentioned separating more than a single sativic acid from the oxidation of linolic acid. However, among others, Fahrion,<sup>16</sup> Krzizan,<sup>17</sup> and Tsujimoto<sup>18</sup> have described acids melting from 152° to 168°. These or some of them, may well have been the  $\alpha$ -acid in various degrees of purity.

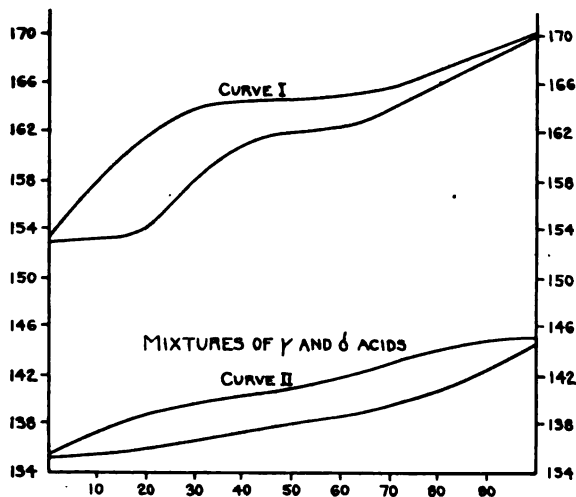


Fig. 1.  
Mixtures of  $\alpha$  and  $\beta$  acids.

**Melting Points of Mixtures of Other Satic Acid.**—In the same way as has been described for the pairs  $\gamma$  and  $\delta$ , and  $\alpha$  and  $\beta$ , the melting points of mixtures of the other 4 pairs were investigated. The results are plotted in Figs. 2 and 3. In each of these 4 cases, the effect of mixing on melting-

<sup>14</sup> Hazura, *Z. angew. Chem.*, 1, 313 (1888).

<sup>15</sup> A. Rollet, *Ref. 12*, p. 420.

<sup>16</sup> Fahrion, *Z. angew. Chem.*, 17, 1483 (1904).

<sup>17</sup> Krzizan, *Chem. Rev. Fett Hartind.*, 15, 8 (1908); 16, 3 (1909).

<sup>18</sup> Tsujimoto, *ibid.*, 18, 112 (1911).

point lowering was distinct, though sometimes rather slight. The  $\beta$ - $\delta$ , and to a lesser degree the  $\alpha$ - $\delta$  combination showed evidence of solid solution formation. The  $\alpha$ - $\beta$  and  $\alpha$ - $\gamma$  mixtures, on the other hand, gave no such indications, the melting points being quite sharp.

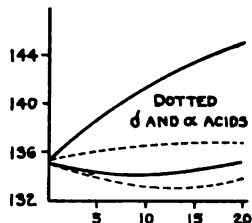


Fig. 2.

Solid curves.

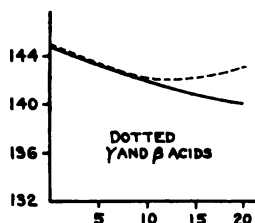
Mixture of  $\delta$  and  $\beta$  acids.

Fig. 3.

Solid curves.

Mixture of  $\gamma$  and  $\alpha$  acids.

**Stability of  $\alpha$ -Sativic Acid.**—Acetic anhydride is recognized as a reagent which in certain cases is capable of bringing about the conversion of one stereo-isomer into another. It was therefore considered worth while to show that the  $\gamma$ - and  $\delta$ -acids were not formed by a mere rearrangement of the  $\alpha$ - and  $\beta$ -forms.

One g. of  $\alpha$ -sativic acid was refluxed with 10 cc. of acetic anhydride and 1 g. of potassium acetate, under the same conditions as were used in the transformation of dibromo-dihydroxy-stearic acid. The product was saponified with aqueous alkali as already described. After one recrystallization, the product (0.75 g.) melted at  $152-3^\circ$ . No transformation, therefore, has occurred, and a further testing of this question would seem superfluous.

### Summary.

1. Two distinct isomeric sativic acids (tetrahydroxy-stearic acids) have been obtained as the chief products of the oxidation of linolic acid by permanganate.
2. The additions of hypochlorous and hypobromous acids to linolic acid have been studied and shown to take place readily and with good yields.
3. These addition products give, on hydrolysis, two additional sativic acids, hitherto unknown.
4. Attention has been called to the fact that there are 4 possible stereo-isomers corresponding to the accepted structural formula for linolic acid. From a consideration of the 4 sativic acids described above, it is shown that only 2 of these isomeric forms occur (at least in important amounts) in linolic acid as usually prepared. It is further indicated that the most probable structures for this pair of isomers are those represented by Formulas II and V, above.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS.]

THE PREPARATION OF DIALKYL MERCURY COMPOUNDS  
FROM THE GRIGNARD REAGENT.

BY C. S. MARVEL AND V. L. GOULD.

Received August 5, 1921.

Although many of the metal alkyls have been prepared by the action of the Grignard reagent on the anhydrous metal halide, this method has not been generally applied to the preparation of the dialkyl mercury compounds. Diphenyl mercury,<sup>1</sup> dicyclohexyl mercury<sup>2</sup> and dibenzyl mercury<sup>3</sup> have already been prepared from the Grignard reagent and mercuric chloride, but only in poor yields. This method, however, may be applied to the preparation in good yields, of various dialkyl mercury compounds. The present paper contains a description of some of these preparations and points out the precautions that must be observed to obtain good results.

Many reactions have so far been used in the preparation of dialkyl mercury compounds, but all give poor results and none is of wide application. The method which has been most commonly and successfully employed is the treatment of an alkyl halide with dilute sodium amalgam in the presence of a catalyst such as ethyl acetate.<sup>4</sup> Even this reaction, however, is limited to primary alkyl halides. As a consequence the mercury compounds with secondary alkyl groups are almost unknown. Di-*sec*-butyl mercury has been prepared by the electrolytic reduction of methyl-ethyl ketone using a mercury cathode,<sup>5</sup> but no simple method has previously been available for preparing this type of mercury compound.

When an excess of the Grignard reagent reacts with a mercuric halide, there is formed first an alkyl mercury halide, which is then converted to the dialkyl mercury compound. The first reaction goes very easily but a large excess of Grignard reagent and long heating are necessary to bring about the second. Either mercuric chloride or iodide may be used without changing the yield of dialkyl mercury compound. Mercurous chloride may also be used, but the yields are always lower than those obtained from the mercuric salts. It is quite necessary to remove any unchanged magnesium from the Grignard reagent before treating it with the mercuric

<sup>1</sup> *Ber.*, 37, 1127 (1904).<sup>2</sup> *Ibid.*, 47, 1655 (1914).<sup>3</sup> *J. Chem. Soc.*, 101, 735 (1912); *Ber.* 46, 64 (1913); 48, 907 (1915); *THIS JOURNAL*, 40, 1266 (1918).<sup>4</sup> *J. Chem. Soc.*, 16, 416, 418, 420 (1863); 19, 150 (1866). *Ann.*, 130, 105, 109 110 (1864); 139, 128 (1866); 154, 199 footnote (1870). *Compt. rend.*, 76, 134 (1873); 77, 1405 (1873). *Jahresber.*, 1873, 517. *J. prakt. Chem.*, [2] 8, 397 (1873). *Ber.*, 12, 1880 (1879); 21, 2037 (1888). *THIS JOURNAL*, 33, 1561 (1911); 40, 1269-71 (1918). *Zentr.*, 1921, III, 26.<sup>5</sup> *Ber.*, 39, 3628 (1906).

halide, or reduction to the mercurous salt occurs and the yields are lowered. When these precautions are observed, dimethyl mercury is formed to the extent of 61–66% of the calculated amount; di-ethyl, 60–63%; di-*n*-propyl, 45–51%; di-*isopropyl*, 60%; di-*n*-butyl, 47%. From these results it can readily be seen that the reaction of the Grignard reagent with mercuric halides to form dialkyl mercury compounds is quite general and is not limited in its application as are the older methods.

An attempt was made to obtain the intermediate alkyl mercury compound which is first formed when the Grignard reagent reacts with mercuric chloride. Methyl-magnesium iodide and an excess of mercuric chloride give methyl mercury iodide in 85–88% yields. However, if an alkyl magnesium bromide reacts with mercuric chloride, a mixture of alkyl mercury chloride and bromide is produced. For example, *n*-butyl-magnesium bromide reacts with an excess of mercuric chloride to give a product melting at 125.5–126°. The melting point is not changed by several crystallizations from alcohol or ligroin. However, the product contains both chlorine and bromine, and a quantitative analysis for carbon showed that it was a mixture of approximately equal parts of *n*-butyl-mercury chloride and *n*-butyl-mercury bromide. The pure chloride (from di-*n*-butyl mercury and hydrochloric acid) melts at 125° and the pure bromide (from di-*n*-butyl mercury and hydrobromic acid) melts at 129°. A mixture containing approximately equal parts of these two substances melts at 125–126° and might easily be mistaken for a pure substance. Similar results were obtained using propyl and *isopropyl* magnesium bromides with mercuric chloride. There is no doubt that pure substances could be obtained in good yields if the halogen of the alkyl halide were the same as that in the mercuric salt.

In a recent report<sup>6</sup> it has been stated that an excess of *n*-butyl-magnesium bromide reacts with mercuric chloride to give *n*-butyl-mercury bromide, mercurous chloride and only small amounts of di-*n*-butyl mercury. In the same article it is claimed that *n*-butyl-magnesium bromide reacts with an excess of mercuric chloride to give *n*-butyl-mercury bromide. In view of the results which have been given above, it is apparent that the statements in the article referred to are based on results obtained without using the proper precautions.

The analyses given in this paper were made by the Parr total carbon method.<sup>7</sup> This method is much more satisfactory for mercury compounds than is an ordinary combustion.

### Experimental.

**Dimethyl Mercury.**—The Grignard reagent was prepared from 180 g. of methyl iodide and 30 g. of magnesium in 500 cc. of dry ether. After filtering the solution

<sup>6</sup> *Science*, **54**, No. 1384, p. 37 (1921).

<sup>7</sup> *THIS JOURNAL*, **26**, 296 (1904).

through glass wool to remove the unreacted magnesium, it was heated to boiling under a reflux condenser of wide bore. One hundred g. of powdered mercuric chloride was added through the condenser in 5 to 10 g. lots over a period of about 45 minutes. The reaction proceeded very vigorously and the mercuric chloride could not be added more rapidly without danger of losing some material through the condenser. Some of the mercuric chloride stuck to the wall of the condenser and had to be pushed down occasionally by means of a glass rod. After all of the mercuric chloride had been added, the reaction mixture was refluxed for 10 to 12 hours to complete the reaction. The solution was then cooled in ice and the excess of Grignard reagent was destroyed by adding through the condenser about 250 cc. of water. The water was added very slowly to keep the reaction from becoming too vigorous. After the water had been added, the ether layer was separated and the water layer extracted once with 100 cc. of ether. The combined ether extract was washed with about 15 to 20 cc. of water, dried over calcium chloride and carefully distilled using a good column. When most of the ether had been removed, the residue was transferred to a smaller flask and the distillation was completed. All of the ether was again distilled in order to obtain the best yields of dimethyl mercury. The average yield was 51 to 56 g. (61–66% of the calculated amount) boiling at 89–92°. In several runs yields of 65 g. (75% of the calculated amount) were obtained. There is always a small amount of methyl mercury iodide left in the distilling flask. The boiling point of dimethyl mercury is given in the literature as 91–92°, 93–96°<sup>9</sup> and 95°.<sup>10</sup> A sample of dimethyl mercury, after careful purification was found to boil at 92° (cor.) under 740 mm. pressure.

The large excess of Grignard reagent and long heating seem to be necessary in order to obtain good yields. Unless the ether was redistilled, the yield was 10–15% lower than the amounts given above. In one run the mercuric chloride was added to the Grignard reagent in the cold. A hard cake separated in the bottom of the flask and a very poor yield of dimethyl mercury was obtained. When the unreacted magnesium in the solution of the Grignard reagent was not removed before adding the mercuric chloride, the yields were lowered.

In one run, using 180 g. of methyl iodide and 30 g. of magnesium, 170 g. of mercuric iodide was substituted for the mercuric chloride. Fifty-two g. of dimethyl mercury was obtained. With the same amount of Grignard reagent, 137 g. of mercurous chloride gave only 27 g. of dimethyl mercury.

**Di-ethyl Mercury.**—This preparation was carried out in essentially the same manner as described for dimethyl mercury, except that mechanical stirring was used. The Grignard reagent from 125 g. of ethyl bromide and 25 g. of magnesium in 500 cc. of anhydrous ether was treated with 97 g. of mercuric chloride. No difficulty was experienced in separating the ether from the di-ethyl mercury. It was found best to distill the product under reduced pressure to avoid decomposition. The yield of di-ethyl mercury boiling at 97–99° under 125 mm. pressure was 55 to 59 g. (60–63% of the calculated amount). The boiling point of di-ethyl mercury is given in the literature as 159° at atmospheric pressure.<sup>11</sup>

When an equivalent amount of mercuric iodide was used in place of the chloride, the yield was not changed.

**Di-*n*-propyl Mercury.**—The Grignard reagent from 21 g. of magnesium and 108 g. of *n*-propyl bromide in 500 cc. of dry ether was treated with 98 g. of mercuric chloride and the reaction mixture worked up as described for the di-ethyl mercury. Forty-seven

<sup>8</sup> *J. Chem. Soc.*, 105, 668 (1914).

<sup>9</sup> *Ann.*, 108, 104 (1858).

<sup>10</sup> *THIS JOURNAL*, 40, 1271 (1918).

<sup>11</sup> *Ann.*, 130, 109 (1864).



to 53 g. (45–51% of the calculated amount) of di-*n*-propyl mercury boiling at 81–84° at 19 mm. was obtained. The boiling point of di-*n*-propyl mercury is given in the literature as 189–191° at atmospheric pressure.<sup>12</sup>

**Di-*isopropyl* Mercury.**—The Grignard reagent prepared from 24.5 g. of magnesium and 130 g. of *isopropyl* bromide was treated with 80 g. of mercuric chloride. The yield of di-*iso*-propyl mercury was 50–51 g. (60% of the calculated amount) boiling at 119–121° at 125 mm.

**Analysis.** Subs., 0.4893: 258.2 cc. of CO<sub>2</sub> (28° and 741.4 mm.). Calc. for C<sub>6</sub>H<sub>14</sub>Hg: C, 25.17. Found: 25.07.

This compound has already been obtained in small quantities by the electrolytic reduction of acetone, using a mercury cathode,<sup>13</sup> but no constants have been recorded.

**Di-*n*-butyl Mercury.**<sup>14</sup>—The Grignard reagent prepared from 21 g. of magnesium and 134 g. of *n*-butyl bromide was heated with 98 g. of mercuric chloride. It was necessary to distill the product a second time to remove all of the *n*-butyl-mercury halide that was carried over in the first distillation. The yield of di-*n*-butyl mercury was 55 to 56 g. (47% of the calculated amount) boiling at 120–123° at 23 mm. About 42 g. of a mixture of mercury butyl halides was left in the distilling flask. The di-*n*-butyl mercury was pure after a second distillation, as is shown by the analysis.

**Analyses.** Subs. 0.3862, 0.3314; CO<sub>2</sub>, 285.7 cc. (32° and 739.4 mm.), 229.5 cc. (34° and 745.2 mm.). Calc. for C<sub>8</sub>H<sub>18</sub>Hg: C, 30.57. Found: 30.54, 30.60.

The boiling point of di-*n*-butyl mercury is given in the literature as 117–118° at 10 mm.<sup>15</sup>

A few cc. of di-*n*-butyl mercury was dissolved in alcohol and a little hydrochloric acid added. After standing overnight, *n*-butyl-mercury chloride had crystallized from the solution. This was filtered with suction and recrystallized from alcohol. Pearly white crystals with a melting point of 125° were obtained. The melting point given in the literature is 125.5°.<sup>15</sup>

**Analysis.** Subs., 0.6000: CO<sub>2</sub>, 226.2 cc. (37° and 741.5 mm.). Calc. for C<sub>8</sub>H<sub>18</sub>HgCl: C, 16.41. Found: 16.24.

In a similar manner *n*-butyl-mercury bromide was prepared and purified. The melting point is 129°; that given in the literature is 128°.<sup>15</sup>

**Analysis.** Subs., 0.6000: CO<sub>2</sub>, 190 cc. (34.5° and 742.2 mm.). Calc. for C<sub>8</sub>H<sub>18</sub>HgBr: C, 14.24. Found: 13.96.

**Methyl-mercury Iodide.**—The Grignard reagent was prepared from 2.4 g. of magnesium and 15 g. of methyl iodide in 50 cc. of anhydrous ether. The ether solution of methyl-magnesium iodide was filtered through a little glass wool to remove any unreacted magnesium. In a flask fitted with a stopper carrying a reflux condenser, dropping funnel and a stirrer running in a mercury seal were placed 30 g. of mercuric chloride and 150 cc. of dry ether. The stirrer was started and the solution of Grignard reagent was added from the dropping funnel at such a rate that the ether refluxed gently. The reaction mixture was refluxed for 1 hour after all of the Grignard reagent had been added. A little water was then added and the ether removed by distillation. About 200 cc. of water and 5 to 10 cc. of conc. hydrochloric acid were added to the residue to dissolve the excess of mercuric chloride and the magnesium compounds formed during the

<sup>12</sup> *Jahresber.*, 1873, 517.

<sup>13</sup> Ref. 5, p. 3626.

<sup>14</sup> While this paper was being written, an abstract of an article describing di-*n*-butyl mercury, *n*-butyl-mercury chloride and *n*-butyl-mercury bromide appeared in *Zentr.*, 1921, III, 26. As the original article was not available for comparison, analyses have been given in order to prove that these compounds were pure.

<sup>15</sup> Cf. Ref. 14.

reaction. The methyl-mercury iodide was filtered with suction and recrystallized from boiling alcohol. The yield was 29 to 30 g. (85-88%). The product was light yellow in color and had a melting point of 142-143°. The melting point given in the literature is 143°. <sup>18</sup>

**Action of *n*-Butyl-magnesium Bromide on an Excess of Mercuric Chloride.**—The Grignard reagent was prepared from 15 g. of *n*-butyl bromide and 2.4 g. of magnesium in 50 cc. of dry ether. This was added to a suspension of 30 g. of mercuric chloride in 150 cc. of dry ether and worked up as described in the preceding experiment. Twenty-five to 26 g. of product melting at 125.5-126° was obtained after recrystallization from alcohol. It may be recrystallized from either alcohol or ligroin without changing the melting point. Qualitative tests show the presence of chlorine and bromine. The quantitative analysis for carbon shows that this product is a mixture of almost equal parts of *n*-butyl-mercury chloride and *n*-butyl-mercury bromide.

**Analyses.** Subs., 0.6000, 0.600: CO<sub>2</sub>, 206 cc. (32.5° and 744.2 mm.), 208 cc. (33.5° and 744.0 mm.). Calc. for C<sub>4</sub>H<sub>9</sub>HgCl: C, 16.41; calc. for C<sub>4</sub>H<sub>9</sub>HgBr: C, 14.25. Found: 15.29, 15.34.

A mixture containing approximately equal parts of pure *n*-butyl-mercury chloride and *n*-butyl-mercury bromide was prepared and the melting point was found to be 125-126°.

*n*-Propyl-magnesium bromide and *isopropyl*-magnesium bromide give similar mixtures when allowed to react with an excess of mercuric chloride.

### Summary.

1. The reaction between an excess of the Grignard reagent and a mercuric halide has been shown to furnish a very satisfactory method for the preparation of di-alkyl mercury compounds, provided the proper precautions are observed.

2. Mercury compounds containing primary and secondary alkyl groups can be prepared by this reaction. Compounds with tertiary alkyl groups could undoubtedly be prepared by the same method.

3. An alkyl magnesium bromide reacts with excess of mercuric chloride to give a mixture of alkyl mercury chloride and bromide. To obtain these compounds pure, the halogen of the alkyl halide must be the same as the halogen of the mercuric salt.

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<sup>18</sup> *Ann.*, 85, 363 (1853).

[CONTRIBUTION FROM THE LABORATORY OF ORGANIC CHEMISTRY OF THE STATE UNIVERSITY OF IOWA.]

## THE NITRATION OF HALOGENATED PHENOLS.

BY L. CHAS. RAIFORD.

Received August 8, 1921.

Armstrong and Harrow<sup>1</sup> found that when 2,4,6-tribromophenol was gradually added to conc. nitric acid (relative amounts employed are not specified) 2 of the halogen atoms were replaced by nitro groups and that the product was 2,4-dinitro-6-bromophenol. In a second experiment, when the trihalogenated phenol was dissolved in glacial acetic acid, one molecular proportion of nitric acid added, and the whole heated for some time on the water-bath, the *para* bromine atom only was displaced, and 2,6-dibromo-4-nitrophenol was obtained. The use of more nitric acid gave the dinitro compound mentioned above.

Claus and Hirsch<sup>2</sup> who studied the action of conc. nitric acid on 2,4,6-tribromo-*m*-cresol in glacial acetic acid solution in the cold, isolated a mononitro-dibromo derivative melting with decomposition at 143°, to which they assigned the structure, 2,6-dibromo-4-nitro-*m*-cresol.

Foster<sup>3</sup> working under the direction of Zincke, found that treatment of a glacial acetic acid solution of 2,4,6-tribromo-*m*-cresol with sodium nitrite gave a yield of 83% of a mononitro-dibromo derivative melting at 128° (Foster says nothing about decomposition upon melting) to which he gave the structure 2,6-dibromo-4-nitro-*m*-cresol, evidently identical with the product obtained by Claus and Hirsch. Zincke<sup>4</sup> has summarized this and similar work done by himself and students on the bromine derivatives of *ortho*, *meta* and *para* cresols, and has reached the conclusion that in the *meta* series this method of nitration gives products in which the halogen atom *para* to hydroxyl is replaced by the nitro group, while in the *ortho* and *para* series the atom *ortho* to hydroxyl is replaced. In no case has he reported the formation of isomeric compounds as the result of a single nitration.

It has long been known that phenol and the cresols, except the *para* compound, usually give when nitrated a mixture of *ortho* and *para* isomerides; but, so far as the author is aware, no one previous to 1910<sup>5</sup> has recorded the formation of isomeric nitro compounds as a result of the nitration of a halogenated phenol. In 1911 Raiford<sup>6</sup> had occasion to prepare

<sup>1</sup> Armstrong and Harrow, *J. Chem. Soc.*, 29, 477 (1876).

<sup>2</sup> Claus and Hirsch, *J. prakt. Chem.*, [2] 39, 61 (1889).

<sup>3</sup> Foster, *Dissertation*, Marburg, 1898.

<sup>4</sup> Zincke, *J. prakt. Chem.*, [2] 61, 561 (1900).

<sup>5</sup> Raiford and Heyl, *Am. Chem. J.*, 43, 393 (1910), and 44, 209 (1910).

<sup>6</sup> Raiford, *Am. Chem. J.*, 46, 417 (1911).

as starting material in another study<sup>7</sup> a considerable quantity of 2,6-dibromo-4-nitro-*m*-cresol (OH=1), and found a modification of Zincke's method of nitration of 2,4,6-tribromo-*m*-cresol the most convenient way of securing the desired product. Following the general directions given by Foster,<sup>8</sup> with the exception that these experiments were carried out at a temperature of 12–15°, and the reaction mixture was poured into water as soon as all nitrite had dissolved,<sup>8</sup> I found that the reaction gave isomeric mononitro-dibromo compounds that were proved very decisively to be 2,4-dibromo-6-nitro- and 2,6-dibromo-4-nitro-*m*-cresols, m. p. 87° and 134° (with decomp.),<sup>9</sup> respectively.

To test the possibilities of this reaction still further, Raiford and Heyl<sup>6</sup> subjected 2,4,6-tribromophenol and the corresponding tri-iodo compound to the action of nitrous acid under the conditions specified above, and found that in each case there were formed isomers in which the *ortho* and the *para* halogen atoms, respectively, were replaced by the nitro group.

In the course of a research now in progress in this laboratory, it was found necessary to prepare considerable quantities of several *ortho*-amino-phenols containing acid-forming substituents, and it was thought that this might be done most easily through Zincke's method, starting with the various halogenated phenols which are readily obtained in good yield and which, according to his experience, are not difficult to purify.

The first product selected for this work was the dibromo-*o*-cresol, first prepared by Werner,<sup>10</sup> and to which Claus and Jackson<sup>11</sup> assigned the structure, 2,4-dibromo-*o*-cresol.

Upson<sup>12</sup> nitrated this compound according to Zincke's method, modified to the extent of allowing the reaction mixture to stand overnight before it was poured into water; the nitro compound was isolated by distillation with steam. His study of the product showed that, in the nitration, the bromine atom *ortho* to hydroxyl had been replaced by the nitro group. In 1906, Zincke and Hedenström<sup>13</sup> nitrated the same dibromo-*o*-cresol, and obtained a product that agreed in melting point and other properties with Upson's compound. Without reference to the work of the latter, and without recording any facts to support their views, Zincke and Heden-

<sup>7</sup> Though this work was not published until 1911, the experimental part of it was done in 1908.

<sup>8</sup> Foster specified no temperature limitations, and allowed his reaction mixture to stand until crystals were deposited.

<sup>9</sup> Though the melting points of these products did not agree with the figures given by previous observers for the same compounds (Claus and Hirsch<sup>3</sup> found 93° for the *ortho* compound and 143° for the *para* isomer, while Foster<sup>2</sup> recorded 128° for the latter one) there is no doubt about the structure and purity of my products.

<sup>10</sup> Werner, *Bull. soc. chim.*, 46, 278 (1886).

<sup>11</sup> Claus and Jackson, *J. prakt. Chem.*, [2] 38, 326 (1888).

<sup>12</sup> Upson, *Am. Chem. J.*, 32, 33 (1904).

<sup>13</sup> Zincke and Hedenström, *Ann.*, 350, 269 (1906).

ström assumed that their product was an *ortho* derivative. Each of the previous workers, however, appears to have overlooked the fact that this nitration gives rise to both *ortho* and *para* isomerides. In the work described below it will be shown that it is possible to isolate from the reaction mixture two mononitro-monobromo-*o*-cresols having the structures 2-nitro-4-bromo-*o*-cresol (m. p. 90–91°) and 2-bromo-4-nitro-*o*-cresol, (m. p. 120° with decomp.).

### Experimental.

The starting material employed in this work was *o*-cresol, obtained by fractionating the purest commercial product obtainable. The fraction boiling steadily at 190° was brominated according to Zincke's<sup>14</sup> method modified to the extent that the product was filtered once just before evaporation of the solvent, and again when the solvent ceased to come over on the water-bath; this removes foreign material which would otherwise contaminate the crystals to be separated eventually. The final liquid, which was thick and viscous, was poured into an evaporating dish and allowed to crystallize by evaporation of the remaining solvent. The product thus obtained melted at 57°, the temperature recorded by Zincke, and was nearly free from color. Repeated crystallization from 50% alcohol gave long silky needles that were free from color, and melted at 58°.

Twenty-six and six-tenths g. of this dibromo derivative was dissolved in about 10 times its weight of glacial acetic acid, and the resulting solution was cooled to about 18°; then 10% more than the calculated weight of sodium nitrite was added in small portions during a period of half an hour. When all of the nitrite had dissolved, the liquid was slowly poured into 6 volumes of cold water, while the mixture was stirred. It was allowed to stand for several hours, after which the yellow solid was removed by filtration, washed with water and dried on clay plate. A yield of 90% was obtained. This material melted at 72–79°, which suggested the possibility of a mixture.<sup>15</sup>

### Separation of the Isomers.

In the first attempt to purify this material, it was subjected to steam distillation as recommended by Upson.<sup>12</sup> The volatile product came over very slowly, and was not pure. Repeated crystallization of the distillate from alcohol gave a product having the melting point and other properties reported by Upson and by Zincke (88°); but further purification in the form of the potassium salt, decomposition of this salt by hydrochloric acid, and final crystallization from alcohol or ligroin, gave yellow needles that melted at 90–91°. In the present work examination of the non-

<sup>14</sup> Ref. 13, p. 275.

<sup>15</sup> A mixture of these isomers, purified as indicated in this paper, melts at 81–115°, with final indication of decomposition.

volatile material yielded an isomeride which was proved (see below) to have the *para* structure.

A method of separating these isomers which is much more satisfactory than that indicated above, was to treat the warm chloroform solution of the crude nitration product with about 4 volumes of ligroin (b. p. 60–70°), and allow the resulting mixture to stand for about 24 hours.<sup>16</sup> During this time, most of the *para* compound crystallized out. After decanting the clear supernatant liquid, which contained the *ortho* compound, the *para* isomer was collected and dried. An average yield of 10 to 12% from several nitrations was obtained. In this condition the material was dark colored, and melted at 110–112° with apparent decomposition. Repeated crystallization from benzene gave lemon-yellow colored blocks, apparently rhombic in shape, and nearly transparent when first removed from the mother liquor. When allowed to stand for some time in the air these crystals lost their transparency, while the blocks appeared to split into a mass of opaque, yellow irregularly-shaped crystals. The compound is soluble in other organic solvents; a portion was crystallized from glacial acetic acid. All samples of the pure product melted at 120° with apparent decomposition.

This product is probably identical with that obtained by Auwers<sup>17</sup> by the bromination of *p*-nitro-*o*-cresol, though he reports that his product separated in "white needles from acetic acid." Apparently by the nitration of *o*-bromo-*o*-cresol, the same compound was obtained by Robertson<sup>18</sup> who got "white crystals before the nitration was complete," and secured the purified product in the form of "white crystals from alcohol." So far as the records go, the identity of the products obtained by these chemists rests solely upon the accepted structures of the starting materials and analyses of the final product for bromine. Neither proved further the structure of his product, and Robertson studied only its potassium salt. In view of these facts and because my product was not "white" and had been obtained from a different starting material and by a method different from that used by either of the previous workers, it was analyzed for bromine, and its identity and structure definitely established by the preparation and study of several of its derivatives.

Subs., 0.1916: AgBr, 0.1596. Calc. for  $C_7H_6O_2NBr$ : Br, 34.46. Found: 34.54.

**The Hydrochloride of 2-Hydroxy-3-bromo-5-aminotoluene**,  $C_7H_6CH_3(OH)Br(NH_2HCl)$ .—Ten g. of the nitro compound described above was dissolved in 30 cc. of alcohol, and reduced with a hydrochloric acid solution of stannous chloride in the usual

<sup>16</sup> Attention is here called to the fact that this method of separation of the isomers that resulted from the nitration of 2-4-6-tribromo-*m*-cresol (*Am. Chem. J.*, **46**, 427 (1911)) caused an immediate precipitation of the *para* isomeride in a nearly pure condition.

<sup>17</sup> Auwers, *Ber.*, **39**, 3174 (1906).

<sup>18</sup> Robertson, *J. Chem. Soc.*, **93**, 788 (1908).

way.<sup>19</sup> The product obtained, which was faintly yellow, was finally secured as perfectly colorless crystals, free from tin salt, after two further crystallizations. The compound is readily soluble in water (difference from the *ortho* compound,<sup>1</sup> see below) and in alcohol. Analysis for halogen agrees with the formula assigned.

*Analysis.* Subs., 0.2056: Ag Hal., 0.2868. Calc. for  $C_7H_5ONClBr$ : Hal., 48.40. Found: 48.60.

**2-Hydroxy-3-bromo-5-aminotoluene**,  $C_6H_4CH_3OHBrNH_2$ .—This free base was obtained by treatment of an aqueous solution of the hydrochloride above described with slightly more than the theoretically required amount of ammonium carbonate solution. The aminophenol, which was promptly precipitated, was quickly collected on a filter, washed with several small portions of cold water, and then dried on clay plate. It melted at 142° with apparent decomposition. From ligroin (b. p. 100–110°) it separated as crystalline plates that had a slight pink color, and that melted at 144°, and turned black.

*Analyses.*<sup>20</sup> Subs. 0.2039, 0.2169: AgBr, 0.1901, 0.2014. Calc. for  $C_7H_5ONBr$ : Br, 39.57. Found: 39.67, 39.51.

**2-Bromo-4-acetyl-amino-6-methylphenyl Acetate**,  $C_8H_8(OCOCH_3)Br(NHCOCH_3)CH_3$ .—This compound was prepared by warming a mixture of 3.3 g. of the hydrochloride mentioned above and an equal weight of anhydrous sodium acetate with a slight excess of acetic anhydride for about 10 minutes. The cold reaction mixture was freed from sodium salts by extraction with water, after which the acetyl derivative was collected on a filter and dried; 3.63 g. was obtained, a yield of 93%. In this condition the product melted at 165–167°, and was nearly pure. Repeated crystallization from ethyl acetate gave short, colorless prisms that were clear and glass-like when seen under the microscope, and which, in masses, viewed with the naked eye, gave a very faint, bluish reflection. The melting point was 169–170°. A sample purified by treatment of a chloroform solution of the compound with two volumes of ligroin (60–70°) gave small colorless flakes that melted at 169°. The substance does not dissolve readily in caustic alkali solution, and was regarded as a di-acetyl derivative. Analysis for bromine was in accord with this view.

*Analysis.* Subs., 0.3391: AgBr, 0.2246. Calc. for  $C_{11}H_{13}O_2NBr$ : Br, 27.95. Found: 28.18.

**2-Hydroxy-3-bromo-5-acetyl-amino-toluene**,  $C_8H_8CH_3(OH)Br(NH.COCH_3)$ .—This product was obtained by removal of the O-acetyl from the di-acetyl derivative described above, by saponification. 0.87 g. of the latter was mixed with 30 cc. of cold water containing 0.25 g. of sodium hydroxide (two equivalents), and the mixture frequently shaken during a period of several hours, after which it was allowed to stand overnight. Nearly all of the solid passed into solution, giving a pink colored liquid. The mixture was next filtered, the residue washed with water and dried. Its melting point (169–170°) and other properties showed that it was unchanged di-acetyl derivative. When the combined filtrate and washings was acidified with hydrochloric acid, a gray solid was precipitated at once. This was collected on a filter, washed with several portions of water and dried on clay plate. The product in this form melted at 154–155°. It was readily soluble in a solution of sodium hydroxide, and from this it was precipitated in the unchanged form by acids; this behavior indicated the presence of a free hydroxyl group. It was further purified by crystallization from benzene, from which it separated in the form of nearly colorless needles. Analysis for halogen is in accord with a formula requiring one acetyl radical.<sup>21</sup>

<sup>19</sup> Ref. 6, p. 419.

<sup>20</sup> I am indebted to Miss E. Mackintosh for these analyses.

<sup>21</sup> I am indebted to Messrs. H. A. Iddles and P. Glavincheff for these analyses.

*Analyses.* Subs., 0.1270, 0.1365: AgBr, 0.0987, 0.1049. Calc. for  $C_6H_4O_2NBr$ : Br, 32.76. Found: 33.06, 32.75.

**Proof of the Structure of the Nitro Compound, Melting at 120°.**

The derivatives prepared and analyzed up to this point show that the nitro compound melting at 120° has the composition assigned to it by Auwers and Robertson. To determine the relative positions of the hydroxide and nitro radicals, a portion of the corresponding amino compound (see above) was prepared and its oxidation product studied. One and two-tenths g. of the amino hydrochloride described above was dissolved in 30 cc. of water containing 3.25 g. of ferric chloride, and the mixture allowed to stand overnight. The solid present at the end of the period was filtered off, washed with water and dried on a clay plate. It weighed 0.75 g. which is a yield of 73%. In this form it melted at 93°, which is the temperature reported by Claus and Jackson<sup>11</sup> for 6-bromo-2-methyl-1,4-benzoquinone. Crystallization from ligroin (b. p. 60–70°) gave orange colored prisms that melted at 95°.

Further identification of the product was obtained by reduction to the corresponding hydroquinone. For this purpose 0.5 g. was ground to a paste with 10 cc. of water, the mixture saturated with sulfur dioxide, warmed until solution took place, cooled to the room temperature, again saturated with the gas, and allowed to stand overnight. The nearly colorless liquid was extracted with ether, the ether distilled, and the remaining viscous, nearly colorless liquid poured on a watch crystal. After a time it set to a mass of slightly bluish irregularly shaped crystals that melted at 115°. Claus and Jackson<sup>11</sup> report 112° as the melting point of this compound. The product was further purified by treatment of a hot saturated benzene solution of the material with two volumes of ligroin, when nearly colorless leaflets were deposited upon cooling. These melted at 117°.

The identity of the latter product was still further established by conversion of a portion of it into a di-acetyl derivative; 0.48 g. was mixed with an equal weight of anhydrous sodium acetate and heated with acetic anhydride. After the product cooled, the sodium salt and unchanged anhydride were removed by water, and the solid was collected on a filter, washed and dried; 0.58 g. was obtained, a yield of 92%. The crude product melted between 75° and 80°. Crystallization from ligroin (100–110°) gave colorless, flat rhombohedrons that melted to a clear colorless liquid at 79°. Claus and Jackson<sup>11</sup> acetylated this hydroquinone and obtained a product that melted at 57° which they did not analyze or study further. My product did not dissolve in a solution of caustic alkali and the analysis for bromine is in accordance with the formula for a di-acetyl derivative.

Subs., 0.2341: Ag Br, 0.1551. Calc. for  $C_{11}H_{11}O_4Br$ : Br, 27.85. Found: 28.19.

The mononitro-monobromo-*o*-cresol melting at 90–91°, which was iso-



lated from the same reaction mixture as that one the derivatives of which have just been described, had previously been prepared by both Upson<sup>12</sup> and Zincke<sup>4</sup> and was identified by the former as an *ortho* compound. The work herewith reported shows that it is isomeric with the product melting at 120° (see above) and which has just been proved to have the *para* structure. My interest in these products lay in the probability that the corresponding amino-cresols, only one of which had hitherto been isolated, and this without the study of any of its derivatives or the proof of its structure, would provide suitable compounds with which to test further the migration of acyl from nitrogen to oxygen previously reported from this laboratory.<sup>22</sup> Accordingly, the reduction products and a few derivatives were prepared.

**The Hydrochloride of 2-amino-4-bromo-6-methylphenol,  $C_6H_4OH(NH_2HCl)-BrCH_3$ .**—This product was obtained by reducing the corresponding nitro compound with stannous chloride in the usual way. It is much less soluble in water than the *para* isomer (see above), which made it necessary to use 50% alcohol in the crystallizations required to free the compound from tin salt. Analysis for halogen showed that the substance was pure.

*Analysis.* Subs., 0.2396: Ag Hal., 0.3349. Calc. for  $C_7H_7ONClBr$ : Hal., 48.40. Found: 48.70.

**2-Amino-4-bromo-6-methylphenol,  $C_6H_4OHNH_2BrCH_3$ .**—A base having this composition and probably this structure was isolated by Claus and Jackson<sup>11</sup> who did not study it further. In my work the product was obtained from the corresponding hydrochloride by triturating a thin paste of this salt and water with the theoretical amount of ammonium carbonate solution until effervescence ceased, and quickly filtering the mixture. After it was dried on clay plate, this material melted at 113°, and recrystallization by treatment of its warm alcoholic solution with water did not change this. Analysis for halogen gave figures that are in accord with the formula assigned.

*Analysis.* Subs., 0.1793: AgBr, 0.1675. Calc. for  $C_7H_8ONBr$ : Br, 39.56. Found: 39.75.

**2-Acetyl-amino-4-bromo-6-methylphenyl Acetate,  $C_6H_3(OCOCH_3)(NHCOCH_3)-BrCH_3$ .**—The base described above was still further characterized by the preparation of its acetyl derivative. 4.77 g. of the hydrochloride was intimately mixed with an equal weight of anhydrous sodium acetate and the mixture warmed for 15 minutes with excess of acetic anhydride. The mass was cooled, powdered and extracted with water to remove sodium salts. The remaining solid was freed from excess of water by suction, and dried; 5.6 g. was obtained, a yield of 84%. In this condition the product melted at 190–193°. Repeated crystallization from alcohol gave colorless, long silky needles that melted at 199–200°. It is readily soluble in other organic solvents but crystallized best from alcohol. It did not dissolve at once in cold solution of caustic alkali, but disappeared slowly, due to saponification at the O-position. This behavior characterizes it as a di-acetyl derivative, which is in agreement with the analysis for bromine.

*Analyses.* Subs., 0.1474, 0.2160: AgBr, 0.0979, 0.1434. Calc. for  $C_{11}H_{12}O_4NBr$ : Br, 27.95. Found: 28.26, 28.25.

### Summary.

1. When the dibromo-*o*-cresol, melting at 58°, is nitrated by treatment

<sup>22</sup> THIS JOURNAL, 41, 2068 (1919).

of its glacial acetic acid solution with nitrous acid, it gives 2 isomeric mononitro-monobromo-*o*-cresols, melting at 90–91° and 120°, respectively. The latter has been proved to have the *para* structure.

2. The amino-cresols corresponding to these nitro compounds will be used in the further study of the migration of acyl from nitrogen to oxygen.

IOWA CITY, IOWA.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY, No. 378.]

## THE QUANTITATIVE DETERMINATION OF THE ANTISCORBUTIC VITAMIN (VITAMIN C).

BY H. C. SHERMAN, V. K. LAMER AND H. L. CAMPBELL.

Received September 2, 1921.

Each vitamin is known by the physiological effects which result from its absence or from the intake of an insufficient quantity. These effects are failure of growth, or development of a deficiency disease, or both. The relative amounts of any one of the vitamins in different foods or in the same food before and after treatment can in general best be measured by feeding a suitable experimental animal, of standard initial age and size, with a basal diet adequate in all other respects but devoid of the vitamin in question, and finding how much of the food under investigation must be fed in order to supply enough of the vitamin to meet the needs of the standard test animal. This is sometimes determined in terms of the proportion in which the food under test when serving as the sole source of the vitamin in question must enter into the food mixture in order to render the food supply adequate in this respect. Or the food to be tested may be fed separately from the basal ration and the minimum quantity of the food which will thus suffice to protect the standard animal from vitamin deficiency may be determined in terms of the actual weight of food thus required as source of vitamin. This latter method is the one chiefly used in studies of the antiscorbutic vitamin and is sometimes referred to as determination of the minimum protective dose. See discussion by Chick and Hume.<sup>1</sup>

Holst and Frölich as early as 1912<sup>2</sup> made comparisons of the antiscorbutic properties of foods by finding whether or not certain arbitrarily chosen quantities which they fed would suffice to prevent the appearance of scurvy; but the basal diet which they employed, consisting usually of oats and water only, was deficient in other respects as well as in antiscorbutic vitamin.

Cohen and Mendel<sup>3</sup> devised a new basal ration planned to provide all necessary nutrients except the antiscorbutic, and showed that experimental scurvy can be induced in the guinea pig at will, and formulated more fully the criteria for the recognition

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<sup>1</sup> Chick and Hume, *J. Biol. Chem.*, 39, 203 (1919).

<sup>2</sup> Holst and Frölich, *Z. Hyg. Infektionsk.*, 72, 1 (1912).

<sup>3</sup> Cohen and Mendel, *J. Biol. Chem.*, 35, 425 (1918).

of this condition. Hess and Unger<sup>4</sup> employed chiefly a basal ration of oats, hay and water.

Chick, Hume, and Skelton,<sup>5</sup> Delf,<sup>6</sup> and other workers at the Lister Institute have used a basal ration of oats, bran and liberal amounts of autoclaved milk. They have done much to establish the importance of quantitative methods in the study of vitamin problems and have recorded a very valuable series of determinations of the antiscorbutic values of different foods; but it is doubtful whether the heat treatment to which they subjected the milk entering into their basal rations can be depended upon to destroy all of the Vitamin C and still leave the diet adequate as regards Vitamin A.<sup>7</sup>

Building upon the experience of the previous investigators as well as upon our studies of both rats and guinea pigs, we have still further developed the basal ration to ensure its freedom from Vitamin C and its entire adequacy in all other respects.

The basal diet as finally adopted is as follows.

	%
Oats, sound whole grain, ground in the laboratory as needed. ....	59
Skimmed milk powder, heated on open trays at 110° until all antiscorbutic vitamin is destroyed. ....	30
Butter fat, freshly prepared. ....	10
Sodium chloride. ....	1
	<hr/> 100

This diet supports excellent growth up to the time of the onset of scurvy.

Sound mature oats show no antiscorbutic property when fed to guinea pigs and are eaten readily by them. By using heated skimmed milk and fresh butter fat instead of heated whole milk, the absence of antiscorbutic vitamin is at least equally well ensured and the palatability of the diet and its fat-soluble vitamin content are improved. The heat treatment necessary to ensure complete destruction of Vitamin C in the skimmed milk powder should be determined by each investigator for his own material and technique, keeping in mind the likelihood of variation in antiscorbutic vitamin content of milk with the season and the importance of eliminating this vitamin completely from the basal ration without subjecting the food to such excessive heating as would give it a burnt taste and prevent its being eaten readily by the experimental animals. In our experiments, 2 hours' heating at 110° in shallow trays freely exposed to the air of the oven was found to be sufficient as determined by controlled feeding experiments.

After such heating the milk powder was of a light buff color. The butter fat, prepared by melting butter of good quality at the lowest possible temperature and freeing from water and curd by decantation and filtration through paper, was intimately mixed with the heated milk powder, the salt, and the freshly ground oats, so that the constituents

<sup>4</sup> Hess and Unger, *J. Biol. Chem.*, 35, 479, 487 (1918).

<sup>5</sup> Chick, Hume and Skelton, *Lancet*, 1918, II, 735.

<sup>6</sup> Delf, *Biochem. J.*, 12, 416 (1918); 14, 211 (1920).

<sup>7</sup> Delf, Ref. 6, pp. 436-42.

of the mixture could not be separated by the experimental animal while eating. The food mixture should be kept in a refrigerator in well-filled, air-tight containers; fresh portions fed daily, and feeding cups thoroughly cleansed at least twice a week, since the slightest incipient rancidity may result in failure of the animals to eat the food readily in which case the interpretation of results will be difficult and probably of very doubtful value.

**Selection and care of experimental animals.**—The experimental animals should either be bred by the investigator or purchased at an early and known age. They should be known to be growing at a normal rate. For about a week before the beginning of the experimental period they should be housed in the experimental cages or pens and fed with the above basal ration plus green food, both *ad libitum*. The experiment proper is then begun by simply discontinuing the green food with or without the feeding of a measured amount of antiscorbutic in addition to the basal ration. Our experience with about 200 of these experimental animals indicates that young guinea pigs 6 to 8 weeks old and weighing 300 to 350 g. are best used for this purpose. Placed at this age and size upon the above basal ration with food and water always available they usually eat about 18 to 20 g. of the dry food mixture per day and continue to grow for about 15 days, then lose weight rapidly and die of scurvy in from 26 to 34 days after being deprived of antiscorbutic food. If the animals are much younger, the results are somewhat less regular; if much older, they are somewhat less susceptible and also less desirable in that they are less likely to show good growth up to the time of onset of scurvy symptoms.

**Symptoms, survival period, and autopsy findings.**—With animals such as have been described, the first symptoms of scurvy appear after about 12 days on the above basal diet. The nature and sequence of the symptoms is so clearly described by Cohen and Mendel<sup>3</sup> and by Hess<sup>4</sup> as not to require discussion here. Loss of weight usually begins soon after the appearance of the first symptoms, though some animals begin to lose weight earlier. On the first or second day of the experimental period there may occur a decrease of body weight due to elimination of bulky intestinal contents from the green food of the fore-period. In such cases the minimum weight of the first or second day is taken as the initial weight of the experimental period. As an accurate weight-curve is helpful in the interpretation of results, each animal should be weighed at least once in 3 days throughout the experimental period. Table I shows the body weights at 3-day intervals of those of our experimental animals which were confined to the basal diet only.

<sup>4</sup> Hess, "Scurvy Past and Present," J. B. Lippincott and Co., 1920.

TABLE I  
WEIGHT IN GRAMS, AT THREE-DAY INTERVALS, OF GUINEA PIGS ON BASAL DIET ONLY

Animal No.	0	3	6	9	12	15	18	21	24	27	30	33
(80)	304	283	280	278	268	271	266	272	270	266	240	212
(12)	305	306	302	301	302	288	274	246	214	197	...	...
139	380	335	351	374	399	413	340	329	260	230	...	...
143	361	368	386	415	432	427	439	344	269	219	...	...
187	335	330	329	330	330	326	337	312	295	274	229	204
190	330	320	328	339	350	350	332	324	290	260	235	206
(191)	324	312	324	309	294	290	271	269	240	227	193	...
193	329	308	313	331	340	350	351	337	319	290	258	182
207	321	330	327	341	343	338	350	301	262	192	...	...
212	330	331	333	337	340	334	321	288	257	201	...	...
215	359	355	363	371	378	393	410	372	326	274	231	197
(216)	334	303	297	300	310	283	275	225	200	...	...	...
(217)	300	295	292	295	281	274	274	272	260	214	188	...
A29	300	313	325	341	352	357	358	350	312	255	215	...
A31	325	340	359	373	378	383	383	365	347	217	195	...
Av. of 15	329	322	327	336	340	338	332	314	275	236	220	200
Av. of 10	337	333	341	355	364	367	362	332	294	241	...	...

Fig. 1 shows a typical weight curve and one constructed from the average weights of the animals included in Table I omitting those whose numbers are enclosed in parentheses. Since the time of reaching a maximum

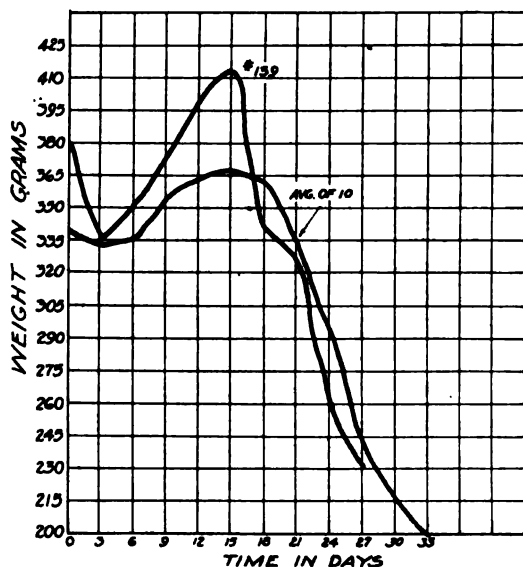


Fig. 1.

and beginning to lose weight differs somewhat with individuals, the effect of averaging the weights is to blunt the typical peak of the weight-curve. The animals whose numbers are enclosed in parentheses did not eat

so well as to show typical gains nor so poorly as to cause them to be rejected entirely.

The survival periods of the animals which we have kept upon the above basal diet only have been as follows: 33, 26, 27, 28, 34, 28, 27, 34, 26, 29, 32, 32, 32, 31, 34 days. At autopsy the findings which proved most

TABLE II

PROTOCOLS OF EXPERIMENTAL ANIMALS ON BASAL DIET ALONE OR WITH ANTISCORBUTIC

Animal No.	Tomato juice Cc.	Initial G.	Body weight Maximum G.	Final G.	Duration of experiment Days	Symptoms
143	0.0	361	439	219	28 <sup>a</sup>	Very severe
193	0.0	329	351	182	34 <sup>a</sup>	Very severe
207	0.0	321	350	192	28 <sup>a</sup>	Very severe
173	1.0	312	405	269	90 <sup>b</sup>	Very severe
184	1.0	321	384	255	53 <sup>a</sup>	Very severe
90	1.4	332	394	201	41 <sup>a</sup>	Severe
93	1.4	321	468	285	63 <sup>a</sup>	Severe
92	1.5	332	368	285	91 <sup>b</sup>	Severe
94	2.0	309	340	311	87 <sup>b</sup>	Moderate
95	2.1	282	388	345	91 <sup>b</sup>	Moderate
155	(a)	320	402	383	73 <sup>b</sup>	Mild
181	(b)	323	503	475	85 <sup>b</sup>	Mild
199	(c)	337	505	492	85 <sup>b</sup>	Very mild
130	(d)	337	415	390	73 <sup>b</sup>	Moderate

## Autopsy Findings

Animal No.	Jaw	Bony system Teeth	Ribs	Joints	Ribs	Hemorrhages Intestine	Joints	Muscles
143	+++	+++	+++	++	++	++	++	++
193	+++	+++	+++	+++	+++	+++	+++	+++
207	+++	+++	+++	+	+++	++	++	++
173	+	-	+++	+++	+++	+	+	+
184	++	++	+++	+++	+++	+	+	++
90	+	+	tr	tr	+	+++	-	tr
93	+	+	+++	+++	+++	+	+++	
92	tr	tr	++	+		+		tr
94	-	-	+	++	-	+	++	tr
95	-	-	?	+	-	-	+	-
155	-	-	+	+		tr	-	-
181	-	-	?tr	-	-	tr	-	-
199	-	-	?+	-	-	+	-	-
130	-	+	++	+	-	+	+	+

(a) Received 3.9 cc. of tomato juice which had been heated for 1 hour at 100°; judged equal to 2.0 cc. of raw juice.

(b) Received 7.0 cc. of tomato juice which had been heated for 4 hours at 100°; judged equal to 2.5 cc. of raw juice.

(c) Received 4.0 cc. of tomato juice which had been heated for 4 hours at 60°; judged equal to 2.5 cc. of raw juice.

(d) Received 2.3 cc. of tomato juice which had been heated for 1 hour at 60°; judged equal to 1.75 cc. of raw juice.

<sup>a</sup> Animal died with scurvy.

<sup>b</sup> Animal was chloroformed for autopsy.

significant were: looseness of teeth, fragility of bones, enlargements and hemorrhages of joints and rib junctions.

**Quantitative Expression of Results.**—The results which we have obtained on feeding the basal diet alone and with the addition of filtered juice of canned tomatoes in measured amounts calculated to the basis of 300 g. of guinea pig per day may be summarized as follows.

*With no antiscorbutic* there is usually good initial growth followed by onset of scurvy symptoms, cessation of growth and great loss of weight before death from scurvy which occurs at 26 to 34 days. Autopsy reveals in severe form all the typical signs of scurvy, notably hemorrhages, fragility of bones, and looseness of teeth. (See Table II.)

*With 1.0 cc. of tomato juice per day* the duration of life is prolonged and becomes less uniform than on the completely scorbutic basal diet. The animals become lame and stiff before death and at death show severe hemorrhages, fragile bones and loose teeth.

*With 1.5 cc. of tomato juice per day* the animals usually live out the experimental period of 70 to 90 days after which it is unlikely that death from scurvy will occur. Scurvy symptoms develop with pain and stiffness in the joints and usually with loss in body weight. Hemorrhages and enlargements of rib junctions may become quite as pronounced as in the previous cases. (Since the animals live longer there is more time for these abnormalities to develop.) Fragility of the bones and looseness of teeth are less marked than when less antiscorbutic is given.

*With 2.0 cc. of tomato juice per day* growth after 15 days is subnormal and animals show soreness of joints without noticeable stiffness. When the animals are killed and examined after 70 to 90 days on this diet they show hemorrhages but not to a pronounced degree. Jaws and teeth appear normal and bones usually so.

*With 3.0 cc. or more of tomato juice per day* there is complete protection from scurvy as judged by examinations both during life and at autopsy. Growth is fully normal in all animals that eat the basal diet well. Hence 3 cc. appears to furnish a fully adequate allowance of the antiscorbutic vitamin.

Table II shows the protocols of typical cases of guinea pigs kept on the basal diet alone or with measured amounts of tomato juice as antiscorbutic. In all cases the volume of tomato juice as stated in the table is the amount which was fed per 300 g. guinea pig. This reduction of the dosage of antiscorbutic to a uniform basis of body weight of standard animal has been found to add considerably to the quantitative significance of the results. Following the precedent of Holst and Frölich the severity of autopsy findings such as hemorrhages and fragility of bones and looseness of teeth are indicated by, – (no different from normal), ? (doubtful), tr (trace), and +, ++, +++ for increasing degrees of severity. From

this series of observations upon animals receiving no antiscorbutic vitamin and with different measured amounts up to the amount which affords complete protection and permits optimum growth it becomes possible to interpret the symptoms and autopsy findings in terms of the percentage of the required amount of antiscorbutic which was actually received by the animal in any individual case. This means that animals fed on this basal diet and receiving some antiscorbutic but not enough for complete protection can be given a quantitative rating based on the weight curve, survival period, and severity of the symptoms and autopsy findings. Thus in comparing the antiscorbutic properties of different foods or of the same food before and after treatment one is not confined entirely to a comparison of the so-called minimum protective dose since the quantitative rating of the degree of protection afforded permits comparisons to be made upon animals receiving less than the amount required for complete protection.

This method has been applied in studying the heat destruction of the antiscorbutic vitamin quantitatively, with feeding experiments to determine how much more of the heated juice must be fed in order to get the same result as with a known quantity of raw juice necessary to give the same degree of protection. This enables one to calculate the amount of antiscorbutic which had been destroyed by the heating.

The last four entries in Table II give the results of experiments of that kind. Following through the findings in the case of No. 155 and comparing them with results above and with the summary given previously, it was considered that on the whole 3.9 cc. of tomato juice heated for one hour at 100° showed practically the same antiscorbutic effect as 2 cc. of the unheated tomato juice and therefore that approximately  $\frac{1}{2}$  of the antiscorbutic vitamin of the tomato juice had been destroyed by the heat treatment. The average of a considerable number of such experiments is practically 50%.

In the next case (No. 181) the animal received 7 cc. of tomato juice heated at 100° for 4 hours. The results indicated that this amount of heated juice was equivalent in antiscorbutic value to 2.5 cc. of raw juice, and the average of a number of such experiments indicated that heating for 4 hours at 100° resulted in the destruction of about 68% of the antiscorbutic vitamin present in the raw juice. The results of experiments on Nos. 199 and 130 (Table II, notes *c* and *d*) show results of heating at 60° with of course a lower rate of destruction than at 100°.

It is plain that in the same way one may compare the antiscorbutic potency of a measured amount of any other material with that of any of the different amounts of canned tomato juice representing any degree of protection up to the complete protection afforded by 3 cc. and can thus determine the relative amounts of antiscorbutic vitamin in different foods



both from experiments in which the exact minimum protective dose is found and from those in which there is a definite partial protection to which a quantitative rating can be given. This method possesses the advantage of the method of minimum protective doses, and in addition permits the use of a numerical value for each individual experiment of a series, the average of which should yield a more trustworthy result than when only those animals receiving exactly the minimum protective dose are taken into account. The data presented in the paper which follows will illustrate the application of this method.

### Summary.

Relative amounts of antiscorbutic vitamin are measured by determining how much of the food under test is required to prevent scurvy in guinea pigs, or by a quantitative rating of the severity of the scurvy produced when less than this "minimum protective dose" is fed. This rating is based upon the weight-curve, duration of life, symptoms, and especially the autopsy findings of guinea pigs of standard initial age and weight. A new basal diet designed to furnish optimum quantities of all essential nutrients other than the antiscorbutic vitamin, and the technique of the experiments, are described.

NEW YORK, N. Y.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY, NO. 379.]

## THE EFFECT OF TEMPERATURE AND THE CONCENTRATION OF HYDROGEN IONS UPON THE RATE OF DESTRUCTION OF ANTISCORBUTIC VITAMIN (VITAMIN C).<sup>1,2</sup>

By V. K. LAMER, H. L. CAMPBELL AND H. C. SHERMAN.

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While the great instability of the antiscorbutic vitamin (Vitamin C) makes it an unpromising material for attempts at actual isolation, the development of methods for measuring relative amounts of this substance with considerable accuracy makes possible the study of its chemical behavior. The present investigation deals with the effects of heating for different lengths of time at 60°, 80°, and 100°, and at different known concentrations of hydrogen ion. As indicated by the earlier work of Delf,<sup>3</sup> the reaction by which Vitamin C is destroyed has a measurable

<sup>1</sup> The data for this paper are taken from a Dissertation submitted by Victor K. Lamer for the degree of Doctor of Philosophy in the Faculty of Pure Science, Columbia University, June, 1921. For the sake of brevity many of the details included in the dissertation are here omitted.

<sup>2</sup> Preliminary reports were presented at the January meeting of the Society of Experimental Biology and Medicine (*Proc. Soc. Exptl. Biol. Med.*, 18, 122 (1921)) and the Rochester meeting of the American Chemical Society, April, 1921.

<sup>3</sup> Delf, *Biochem. J.*, 12, 416 (1918).

velocity, which velocity is accelerated by rise in temperature though less rapidly than most chemical reactions.

The experiments of Harden and Zilva,<sup>4</sup> and Hess and Unger<sup>5</sup> have also shown that the addition of alkali to orange juice reduces the stability of the antiscorbutic vitamin.

In view of the fact that in a later paper Delf<sup>6</sup> states "that neutralizing nearly all of the excess acid in orange juice therefore does not appreciably reduce the stability of the antiscorbutic constituent of the juice at 100°," it was considered that an investigation of the rate of destruction at various measured hydrogen-ion concentrations under definite conditions of time and temperature of heating would be desirable.

In the experiments described it is believed that the influence of these factors has been measured quantitatively with a probable error of less than 5% for each of the chief points determined.

### Selection and Preparation of Antiscorbutic Materials.

The juice from canned tomatoes was selected as the source of Vitamin C in this investigation for the following reasons.

(1) It contains a high concentration of this vitamin, 3 cc. sufficing to give complete protection to a guinea pig, which is an important point in quantitative feeding work since it permits one to reduce the concentration of active material to 10% or even less of its original value and yet not require the administration of an excessive volume in order to attain the same degree of protection as the untreated product affords.

(2) It is possible to eliminate in a large measure the variation in initial antiscorbutic content due to seasonal or other causes, by purchasing the canned tomatoes in case lots.

**Preparation of Materials.**—The material used in feeding was prepared at 5-day intervals by opening one or more cans of tomatoes, and filtering at 10°, first through muslin and then through filter paper. The filtrate, which possessed at most only a slight opalescence, was measured into Erlenmeyer flasks made of Pyrex glass, heated rapidly over a wire gauze with constant swirling until it had attained the desired temperature (which required 1 to 2 minutes) and then at once put into a constant temperature bath accurate to  $\pm 0.2^\circ$ . The evaporation which occurred through the cotton stoppers was noted and either replaced by addition of sterile water, or a correction for the concentration resulting thereby was made in calculating the dosage of the heated juices.

At the end of the heating period, the flasks were cooled quickly (1 to 2 minutes) by means of running water and then placed on ice. All anti-

<sup>4</sup> Harden and Zilva, *Lancet*, II, 320 (1918).

<sup>5</sup> Hess and Unger, *J. Biol. Chem.*, 38, 297 (1918).

<sup>6</sup> Delf, *Biochem. J.*, 14, 220 (1920).

scorbutic material, whether in cans or flasks, was kept at 10° at all times, except for the period of heating indicated. Bacterial action was very carefully avoided.

In all, 4 lots of canned tomatoes were used, each of which was standardized independently, 23 animals being used for this purpose.

In order to test the influence of hydrogen ions or their reciprocal, hydroxyl ions, samples of tomato juice of different degrees of acidity or alkalinity were prepared. The normal hydrogen-ion concentration of the juice from different lots was found to lie between  $10^{-4.18}$  and  $10^{-4.37}$ . When the juice was heated in a boiling water-bath for an hour the hydrogen-ion concentration remained practically unchanged, namely  $10^{-4.18}$  before, to  $10^{-4.23}$  after heating. When the samples were made slightly alkaline difficulty was encountered in maintaining a constant hydrogen-ion concentration due to the fact that at 100° the sugars present are attacked by the hydroxyl ions, yielding organic acids, as the work of Nef<sup>7</sup> has shown, which tends to reduce the alkalinity. A certain amount of discoloration occurred which is very likely due to caramelization of the sugars. Table I shows these effects.

The preparations designated as I, II, III were made by adding the amount of sodium hydroxide indicated in Table I, or its equivalent, per 100 cc. of freshly filtered tomato juice, and heating for 1 hour at 100°. When the period of heating had expired the preparations were at once cooled under the tap in exactly the same manner as the preparations to which no alkali had been added. An amount of hydrochloric acid equivalent to the sodium hydroxide was next added to neutralize the latter so that the effects of the addition of alkali would take place only during the period of heating. Inasmuch as previous workers have not re-acidified after heating the alkaline preparations it was thought advisable to determine whether this might have any influence upon the results.

Preparation III was accordingly divided into two parts at the conclusion of the heating period; IIIa being re-acidified as usual, while in the case of IIIb the preparation was allowed to remain in its alkaline condition at the usual temperature of 10° for the period of 1 to 5 days, during which it was administered daily to the animals of that series.

The changes in volume due to the addition of acid or alkaline solutions were taken account of in all calculations. The hydrogen-ion concentrations were determined electrometrically with the apparatus described by Thomas and Baldwin.<sup>8</sup>

<sup>7</sup> Nef, *Ann.*, 403, 204 (1914).

<sup>8</sup> Thomas and Baldwin, *THIS JOURNAL*, 41, 1990 (1919).

TABLE I

HYDROGEN-ION CONCENTRATIONS OF PREPARATIONS TO WHICH SODIUM HYDROXIDE HAS BEEN ADDED

Prep. No.	0.2 N NaOH per 100 cc. of tomato juice Cc.	Log. of $C_H +$	Remarks
I	11.0	- 5.20	before heating.
I	11.0	- 4.88	after heating 1 hr. at 100°.
II	37.0	- 9.14	before heating.
II	37.0	- 7.53	after heating 1 hr. at 100°.
III (a,b)	74.0	-10.88	before heating.
III (a,b)	74.0	- 8.26	after heating 1 hr. at 100°.

The solutions described were fed to experimental animals (guinea pigs) and the percentage destruction of the vitamin measured by the method described in the preceding paper<sup>9</sup> with the average results shown in Tables II and III.

TABLE II

THE DESTRUCTION OF ANTISCORBUTIC VITAMIN AT HYDROGEN-ION CONCENTRATION EQUAL TO  $10^{-6.18}$  TO  $10^{-6.17}$  (NATURAL REACTION OF TOMATO JUICE). TIME AND TEMPERATURE VARIED.

No. of expts.	Time Hours	Temp. °C.	Average destruction %
12	1	100	50.2±1.3 <sup>a</sup>
3	2	100	58. (about)
11	4	100	67.7±0.9 <sup>a</sup>
6	1	80	40.5±1.2 <sup>a</sup>
5	4	80	53.0±1.3 <sup>a</sup>
5	1	60	25.2±1.0 <sup>a</sup>
6	4	60	36.8±1.5 <sup>a</sup>

<sup>a</sup> See discussion following on probable errors.

TABLE III

DESTRUCTION OF ANTISCORBUTIC VITAMIN IN TOMATO JUICE AT VARIOUS HYDROGEN-ION CONCENTRATIONS. SODIUM HYDROXIDE SOLUTION ADDED AND MATERIAL HEATED FOR 1 HOUR AT 100°, FOLLOWED BY RE-ACIDIFICATION WITH HYDROCHLORIC ACID AT EXPIRATION OF HEATING PERIOD, EXCEPT IN THE CASE OF PREPARATION IIIb WHICH WAS ALLOWED TO REMAIN ALKALINE AFTER HEATING AND FED OVER A PERIOD OF 5 DAYS. ALL PREPARATIONS WERE PRESERVED AT 10°.

Prep.	No. of expts.	Log. $C_H +$ before heating	Log. $C_H +$ after heating	Destruction %
Natural reaction	12	- 4.3	-4.3	50.2±1.3 <sup>a</sup>
I	4	- 5.2	-4.9	58.3±0.7 <sup>a</sup>
II	5	- 9.2	-7.5	61.8±0.8 <sup>a</sup>
IIIa	2	-10.9	-8.3	61-65 (about)
IIIb	3	-10.9	-8.3	90-95 (about)

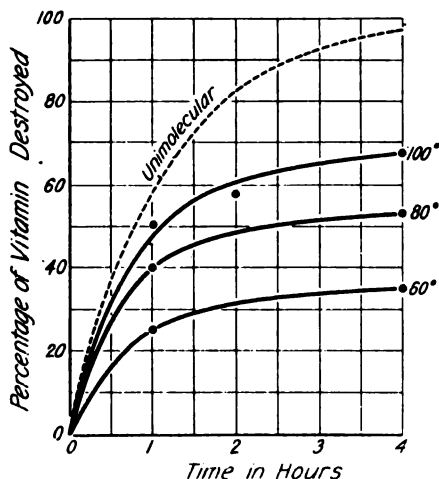
<sup>a</sup> See discussion following on probable errors.

<sup>9</sup> Sherman, LaMer and Campbell, THIS JOURNAL, 44, 165 (1922).

### Discussion of Results.

**Errors Involved.**—The experimental errors in the temperature of heating ( $\pm 0.2^\circ$ ) are negligible, inasmuch as the temperature coefficient as shown later is of the low order of 1.2. The maximum possible error in time of heating could not exceed 4 minutes in 60, or 6.6%; and where this procedure is repeated as many as 18 times for a single experiment the probable error through laws of chance should be very much less. In the case of 4 hours' heating the effect of this error is still further reduced. The error in feeding was of the order of 2 to 3%. The largest error involved in the work is that due to variation of experimental animals.

Inspection of the individual data<sup>10</sup> shows that the maximum variation for single experiments is about 15%. The average of these data and the numbers of experiments are given in Tables II and III. The "probable errors" given were calculated by the usual formula, but it should be stated that they are included only for the purpose of giving an idea of the degree of variation in the results of a given series, since in some of the series the number of experiments was not sufficient to warrant giving them the strict interpretation of a probable error. The general concordance of the values given, however, would indicate that the probable error of the average due



to animal variation is less than 5%.

**The form of the time curve of destruction.**—When the percentage destruction from Table II is plotted against the time as we have done in Fig. 1, it is at once apparent that the destruction of the antiscorbatic vitamin is not dependent upon any one critical temperature, but that the degree of destruction is a function of both the time and the temperature. Further examination shows that it is not possible to express the relationship between these two factors by any of the simple equations of chemical kinetics. If an attempt is made to fit a curve of the unimolecular type it is evident that there is a very marked tendency for the curve to flatten with the progress of time. At 100° the values for  $k$  in the equation

$$\frac{1}{t} \log \left( \frac{1}{1-x} \right) = k$$

<sup>10</sup> Table V, Ref. 1, Dissertation.

(where  $x$  is the fraction changed at the time  $t$ ) are 0.303 at 1 hour, 0.187 at 2 hours, and 0.123 at 4 hours.

Nor do the curves follow the square-root law of Schutz, for in the latter case the destruction at 4 hours should be double that at 1 hour, but instead the destruction seems to be more nearly a function of the 4th root of the time. Thus when we calculate  $K$  by substituting the data from Table III in the equation

$$K = \frac{x}{\sqrt[4]{t}} \quad (\text{where } x \text{ and } t \text{ have the significance given above})$$

we find values which are very nearly constant for the different temperatures.

Thus  $K_{100}^{\circ}$  1 hour, 0.50; 2 hours, 0.49; 4 hours, 0.48. Av.  $K_{100}^{\circ}$ , .49.  $K_{80}^{\circ}$  1 hour, 0.40; 4 hours, 0.38. Av.  $K_{80}^{\circ}$ , 0.39.  $K_{60}^{\circ}$  1 hour, 0.25; 4 hours, 0.26. Av.  $K_{60}^{\circ}$ , 0.255.

It was considered at the outset that it was more important for the purposes of this investigation to obtain reliable representative data at different temperatures than it was to obtain a great many data at any one temperature, and for that reason we have tried to establish only two points on a given temperature curve but to establish these as accurately as possible by the use of an adequate number of animals.

It is interesting to note that this flattening of the reaction curve is frequent also in reactions catalyzed by enzymes such as the hydrolysis of lactose by lactase,<sup>11</sup> the digestion of casein<sup>12</sup> by trypsin, and the action of amylases on starch.<sup>13</sup>

**The temperature coefficient.**—Using the values of  $K$  obtained above for substitution in the equation

$$Q_{10} = \sqrt{\frac{K_{t+20^{\circ}}}{K_t}}$$

we obtain the following values for the temperature coefficient for the intervals for 60° to 80°, and 80° to 100°.

$$Q_{10}(60^{\circ} \text{ to } 80^{\circ}) = 1.23$$

$$Q_{10}(80^{\circ} \text{ to } 100^{\circ}) = 1.12.$$

Delf<sup>3</sup> in her paper upon the destruction of the antiscorbutic vitamin in cabbage leaves offers the value of 1.3 for  $Q_{10}$  from 60–100° as a rough approximation made on the assumption that the velocity is uniformly accelerated throughout its course. As far as the authors are aware this is the only statement in the literature regarding the quantitative relation between the temperature and the velocity of the reaction.

<sup>11</sup> Armstrong, *Proc. Roy. Soc.*, (London), 73, 500 (1904).

<sup>12</sup> Bayliss, "Nature of Enzyme Action," Longmans, Green and Co., 4th Ed., p. 81, for this and other similar work.

<sup>13</sup> Sherman and J. C. Walker, *THIS JOURNAL*, 39, 1476 (1917).

Delf considers this low temperature coefficient to be evidence that the vitamin is neither an enzyme nor a protein, for the temperature coefficients of the inactivation or denaturation of such substances have been found to be extremely high, *i. e.*, of the order  $Q_{10}=7$  (heat destruction of emulsin,<sup>14</sup>) to 635 (coagulation of egg albumin,<sup>15</sup>). We agree fully with this view and would also point out that the temperature coefficient observed corresponds almost exactly with that of a diffusion<sup>16</sup> process.

This fact coupled with the fact that tomato juice is of a colloidal (2-phased) nature furnishes presumptive evidence, at least, that in the heat destruction of antiscorbutic vitamin we are dealing with a heterogeneous reaction.<sup>17</sup>

Reactions having temperature coefficients of this order (1.2) are sometimes explained on the ground that a part of the reaction is photochemical in nature. Experiments in which the material was heated at 60° for 1 hour and exposed at the same time to the light from 4 adjacent 500-watt heater lamps showed no increase in destruction over their controls. This is in harmony with Zilva's<sup>18</sup> negative results in which the ultra-violet rays from a quartz mercury lamp were used.

It may be properly asked whether or not the flattening of the reaction curve can be explained on the basis of the tendency to reach an equilibrium point due to the mass-action effect of the products on the velocity of the reverse action, as has been shown to be the case in the hydrolysis of lactose and for the system glycerol : glucoside : emulsin investigated by Dietz.<sup>19</sup>

The principal objection to the acceptance of this point of view lies in the fact that the equilibrium point if there is one must be capable of being shifted from say 75% to 95% of completion by the simple addition of dilute sodium hydroxide causing a change in hydrogen-ion concentration from  $10^{-4.8}$  to about  $10^{-10}$ . See Table III.

Our results would warrant the general view that for short periods of time (1 hour or less) the extent of the deleterious influence of heating depends more upon the length of time than it does upon the intensity of the process, while for longer periods (4 hours or more) the effect of the intensity assumes greater prominence in comparison to the time than it did in the shorter period. Thus on heating for 30 minutes, it would

<sup>14</sup> Tammann, *Z. physik. Chem.*, 18, 426 (1895).

<sup>15</sup> Chick and Martin, *J. Physiol.*, 40, 404 (1910).

<sup>16</sup> Ohlman (*Z. physik. Chem.*, 50, 309 (1905)) found the temperature coefficient of the diffusion of the common salts, acids and bases to lie between 1.19 and 1.28.

<sup>17</sup> See Lewis, "System of Physical Chemistry," Longmans, Green and Co., 2nd Ed., Vol. 1, Chap. X; and Bayliss, Ref. 12, for a discussion of the kinetics of heterogeneous reactions.

<sup>18</sup> Zilva, *Biochem. J.*, 13, 164 (1919).

<sup>19</sup> Dietz, *Z. physiol. Chem.*, 52, 279 (1907).

appear from Fig. 1 that between 27% and 30% of the vitamin is destroyed, whether at 80° or 100°, whereas at the end of 4 hours' heating, the differences are more pronounced for the same temperatures, namely, 53% and 68%.

**Effects of decreased hydrogen-ion concentration.**—The effects of changed hydrogen-ion concentration are in accordance with the view generally held, since the publication of Holst and Frölich's work, that the vitamin is more stable in acid than in neutral or alkaline solution. The data indicate that neutralization of less than  $\frac{1}{2}$  of the natural acidity (bringing the solution to a hydrogen-ion concentration of  $10^{-5.5}$ ) produces a significant change in the velocity of destruction; namely 58% is destroyed instead of 50%. When the tomato juice is first made distinctly alkaline to phenolphthalein with carbon dioxide-free sodium hydroxide, and after heating one hour at 100° is re-acidified with an amount of hydrochloric acid equivalent to the alkali originally added, we find that the destruction is increased to 61%.

On the other hand when we omit the re-acidification (Prep. IIIb) we get a very much greater effect, due in all probability to the continued destructive action of the hydroxyl ions at 10°. The latter result is in accord with the work of Harden and Zilva<sup>4</sup> who found that orange juice made 0.05 *N* alkaline to phenolphthalein (our Preparation III was 0.0244 *N* alkaline) gave partial protection when fed the same day, but no protection after standing for 24 hours. Hess and Unger<sup>1</sup> report similar results, but neither investigator states the exact temperature employed.

**Oxidation and Reduction.**—Following the completion (March, 1921) of the experimental work given in the preceding tables, 5 papers have appeared in rapid succession dealing with the effect of various oxidizing agents upon the destruction of Vitamin C.<sup>20, 21, 22, 23, 24</sup> The data given show that drastic oxidizing agents such as potassium permanganate and hydrogen peroxide destroy more or less vitamin at room temperature, and that when de-citrated lemon juice is aerated at 100° for 2 hours the destruction is marked. From these papers some have gained the impression that the destruction process is of a purely oxidative nature and that the sole effect of heat is to increase the rate of this oxidation reaction. In order to test this point guinea pigs were fed doses of 2, 3 and 4 cc. of tomato juice, at hydrogen-ion concentrations of  $10^{-4.5}$  and  $10^{-5.5}$ , into which oxygen had been bubbled at atmospheric pressure while it was being heated at 100° for 1 hour. Other preparations were treated in a like manner except that hydrogen was bubbled through them instead of oxygen. The

<sup>20</sup> Hess, *Proc. Soc. Exptl. Biol. Med.*, 18, 143 (1921).

<sup>21</sup> Zilva, *Lancet*, I, 478 (1921).

<sup>22</sup> Ellis, Steenbock and Hart, *J. Biol. Chem.*, 46, 367 (1921).

<sup>23</sup> Anderson, Dutcher, Eckles and Wilbur, *Science N. S.*, 53, 446 (1921).

<sup>24</sup> Dutcher, Harshaw and Hall, *J. Biol. Chem.*, 47, 483 (1921).



preliminary results obtained from 13 animals indicate complete destruction in both the acid and alkaline preparations in which oxygen was used. Where hydrogen was used the degree of destruction was greater than in the experiments quoted in Tables II and III, which would support the contention that the destructions measured in those tables are primarily those of a heat effect *per se* and not of atmospheric oxidation. That destruction by atmospheric oxygen could have played only a minor rôle in the experiments tabulated above becomes more apparent when we consider that the amount of dissolved oxygen available for such a reaction must of necessity be considerably reduced since it is in equilibrium with a gaseous mixture immediately above the liquid in which the air originally present has been displaced by the water vapor coming from the nearly boiling solution, a condition radically different from the case where oxygen or air is bubbled directly into the hot liquid.

It is entirely possible that the heat destruction of Vitamin C is of the nature of an intramolecular oxidation and reduction such as occurs when aldehydes or sugars are heated, especially in alkaline solution. The addition of external oxidizing or reducing agents then would serve to aid in the speed and completeness of the reaction. The writers intend, when more data are available, to discuss the question of vitamin oxidation from the standpoint of oxidation and reduction potentials, particularly in regard to the effect of hydrogen-ion concentration upon the magnitude of these potentials.

### Summary.

1. The effect of heating upon the destruction of the antiscorbutic vitamin in tomato juice has been measured quantitatively ( $\pm 5\%$ ) for periods of 1 to 4 hours, at  $60^\circ$ ,  $80^\circ$  and  $100^\circ$ .

2. The results show that the velocity of destruction, under the conditions of the experiments, decreases with the time and in greater degree than would be expected if the reaction followed the unimolecular law or the square root rule of Schütz. The percentage destroyed varied empirically as the 4th root of the time.

3. The temperature coefficient is of low order:

$$Q_{10} (60-80^\circ) = 1.23; Q_{10} (80-100^\circ) = 1.12.$$

The reaction is not appreciably sensitive to ordinary light. It is probably of the heterogeneous type.

4. The effect of reducing the hydrogen-ion concentration from  $C_{H^+} 10^{-4.3}$  to  $C_{H^+} (10^{-5.3} \text{ to } 10^{-4.9})$  is to increase the destruction during 1 hour at  $100^\circ$  from 50% to about 58%. When the material was made faintly alkaline,  $C_{H^+} (10^{-10.9} \text{ to } 10^{-8.3})$ , the destruction was 61-65%.

5. When re-acidification after heating in alkaline solution ( $C_{H^+} 10^{-10.9}$

to  $10^{-8.3}$ ) was omitted, and the material allowed to remain alkaline at  $10^\circ$  and fed over a period of 5 days, the destruction rose to 90-95%.

6. The possibility of oxidation and reduction in these and other experiments is discussed.

NEW YORK CITY.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF NEBRASKA.]  
**THE PREPARATION AND PROPERTIES OF SEVERAL PHENYL  
ALKYL SUCCINIC ACIDS.**

By FRED W. UPSON AND T. J. THOMPSON.<sup>1</sup>

Received September 6, 1921.

The original purpose of this investigation was the separation of the optical isomers of *isopropyl-phenyl-succinic acid* prepared by Avery and Upson.<sup>2</sup> To the present time this has not been accomplished although resolution was attempted with brucine, quinine, strychnine and cinchonine. During the course of the attempted resolutions, however, a number of incidental questions arose. Among these were the preparation of other substituted succinic acids, the difficulty of saponification of the nitrils of certain substituted succinic acids already referred to by Avery and Upson, and the structure of the sodium benzyl compound which results from the interaction of sodium amide and benzyl cyanide.

### I. Preparation of Nitrils.

Preparation of alkyl phenyl-succino-nitril and of alkyl phenyl-succino-half-nitril half-ester was carried out by condensing alkyl cyanohydrines with benzyl cyanide by means of (1) sodium ethoxide, or methoxide and (2) esters of  $\alpha$ -bromo fatty acids with benzyl cyanide by means of sodamide, respectively.

**1. Alkyl Aldehyde Cyanohydrines with Benzyl Cyanide. Discussion.**—When it was determined that *isopropyl-phenyl-succinic acid* could not be resolved, an attempt was made to prepare other substituted succinic acids, in the belief that optically active compounds might be resolved from them. The method of condensation employed was a modification of the one used by Avery and Upson<sup>2</sup> in the preparation of *isopropyl-phenyl-succino-nitril*. The condensations of the cyanohydrines of acetic aldehyde, *n*-propionic aldehyde, acetone, methylethyl-ketone and *isovaleric aldehyde* with benzyl cyanide were attempted in the order mentioned; but *isovaleric-cyanohydrine* was the only one that gave a condensation compound. The yield was very good in the case of the *isovaleric-phenyl-succino-nitril*; also in the case of *isopropyl-phenyl-succino-nitril*. As yet we

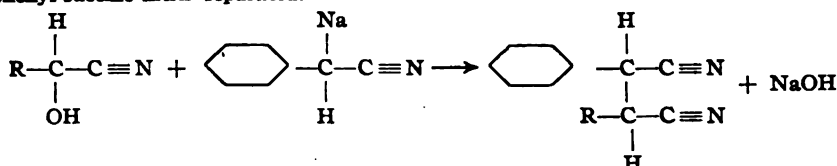
<sup>1</sup> The dissertation upon which this paper is based was presented by T. J. Thompson as partial fulfilment of the requirements for the degree of Doctor of Philosophy in the University of Nebraska.

<sup>2</sup> Avery and Upson, *THIS JOURNAL*, 30, 600 (1908).

have been unable to determine why we could not secure favorable results from the other cyanohydrines. It was first thought, as suggested by Higson and Thorpe,<sup>3</sup> that the proportional amount of sodium used was too large, but this was reduced far below the equimolecular proportion with the same results.

**Experimental.**—Since the operations in each case were in the main the same, only the condensation of *isovaleric*-cyanohydrine with benzyl cyanide will be described.

Eight g. of benzyl cyanide was added to 1.5 g. of sodium, which had been dissolved in an excess of methyl alcohol. To the sodium methoxide-benzyl cyanide solution, 8 g. of *isovaleric*-aldehyde-cyanohydrine was added. The mixture was shaken several times and allowed to stand for several hours, whereupon large crystals of the *isobutyl*-phenyl-succino-nitril separated.

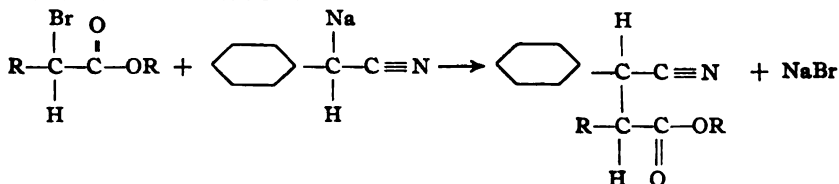


When it was believed that crystallization was complete, the crystals were collected, and dissolved in hot methyl alcohol. After this solution cooled, water was added until crystallization of the nitril occurred. The crystals were dried and weighed. Yield, 84%, much better than the yield obtained by Avery and Upson. Ethyl alcohol may be used in place of methanol, but is slower in reaction and the yield is slightly less.

## 2. Ethyl Esters of Alpha-bromo Fatty Acids with Benzyl Cyanide.

**Discussion.**—In 1910 Bodroux and Taboury<sup>4</sup> allowed sodamide to react with benzyl cyanide suspended in ether. By means of the reaction of alkyl halides on this sodium benzyl cyanide, they were able to prepare a number of derivatives. This method was adapted to the preparation of the substituted succinic acids, if  $\alpha$ -bromo fatty acid esters were used in place of alkyl halides. In each reaction attempted, more or less satisfactory results were obtained. The yield was generally quite low.

**Experimental.**—Four g. of finely powdered sodamide was suspended in 40 cc. of absolute ether and to this 12 g. of benzyl cyanide was added in small amounts while the reaction mixture was cooled by running water. A moderate reaction occurred. Ammonia was evolved and the solution assumed a color varying from amber to red. After the reaction had subsided, the mixture was refluxed for 12 hours. To the sodium benzyl cyanide compound 21 g. of ethyl  $\alpha$ -bromo-*isovalerate* was added in small amounts while the reaction flask was cooled in running water. After a vigorous reaction, the mixture set to a jelly-like mass. A large excess of absolute ether was added and the mixture was refluxed for 24 hours.



<sup>3</sup> Higson and Thorpe, *J. Chem. Soc.*, 89, 1455 (1906).

<sup>4</sup> Bodroux and Taboury, *Compt. rend.*, 150, 531-3 (1910).

When the reaction was complete, the ether solution was acidified with dil. hydrochloric acid. At this point, when an excess of sodamide was added, crystals of the half acid or dibasic acid separated. Whether they were the half-acid, or the dibasic acid, depended upon the character of the substituted groups. This will be discussed later. Usually an excess of sodamide was avoided and the acid solution was extracted several times with ether. Evaporation of the ether under diminished pressure on the boiling water-bath left an oily viscous residue in the flask. When conc. hydrochloric acid was added and the condensation product was refluxed for 8 hours, most of the oily residue disappeared; and, as the product cooled, small crystals separated. Since these crystals were insoluble in benzol, it was possible to extract the non-hydrolyzed residue, to evaporate the benzol under diminished pressure, and to continue the hydrolysis as before. Then the crystals were filtered from the diluted hydrochloric acid solution, dried, and dissolved in hot alcohol. The alcohol solution was cooled and water added, whereupon crystals separated; m. p. (uncorr.)  $172^{\circ}$ . Titration of 0.0910 g. required 38.3 cc. of 0.01 *N* sodium hydroxide solution; the calculated amount for one hydrogen is 41.7 cc.

The crystals gave a positive test for nitrogen. The titration indicated that the compound had been hydrolyzed only partially. Since irregularity in saponification had already been observed,<sup>3</sup> the half-acid was placed in a bomb tube with conc. hydrochloric acid and heated at  $135^{\circ}$  for 24 hours. The crystalline substance obtained was washed into a beaker, and diluted with water to dissolve ammonium chloride. The crystals were then collected and dissolved in the smallest amount of hot alcohol. The addition of a large amount of cold water caused a copious crop of crystals to separate which melted sharply at  $178^{\circ}$ . Titration of 0.0722 g. required 59.0 cc. of 0.01 *N* sodium hydroxide solution; the calculated for two replaceable hydrogens is 61.2 cc. The yield was poor. A qualitative test for nitrogen was negative.

A mixed-melting-point determination was made with the acids obtained from ethyl  $\alpha$ -bromo-*isovalerate* and *isobutyl*-aldehyde-cyanohydrine condensation compounds with benzyl cyanide. This mixture melted sharply at  $178^{\circ}$ , and therefore the compounds resulting from the two methods of preparation are identical.

When the hydrolysis was not attempted by means of refluxing but the oily residue was placed immediately in the bomb tubes, the crystals were found to be enveloped in an oily viscous mass which could be removed by shaking them with benzene.

This same method has been applied in the preparation of the following new substituted succinic acids, in addition to the one already discussed: (1) *n*-propyl-phenyl-succinic acid, prepared from ethyl  $\alpha$ -bromo-*n*-valerate and benzyl cyanide; (2) ethyl-phenyl-succinic acid, prepared from ethyl  $\alpha$ -bromo-*n*-butyrate and benzyl cyanide; (3) methyl-phenyl-succinic acid, prepared from ethyl  $\alpha$ -bromo-propionate and benzyl cyanide.

## II. Saponification.

**Discussion.**—It had been observed by Avery and Upson that the saponification of *isopropyl*-phenyl-succino-nitril was difficult. A similar difficulty of saponification of diphenyl-succino-nitril has been noted by a number of investigators.<sup>4</sup> So far as we have been able to determine,

<sup>4</sup> Reimer, (*Ber.*, 14, 1802 (1881)) in speaking of saponifying dicyano-dibenzyl says: "Upon heating with alcoholic potassium hydroxide the substance yielded besides a resinous product only a very slight amount of acid..... A more successful saponification was accomplished by heating with concentrated hydrochloric acid at  $200^{\circ}$ ."

Chalonay and Knoevenagel (*Ber.*, 25, 289 (1892)) say: "By heating the substance

diphenyl-succino-nitril has never been hydrolyzed satisfactorily except under pressure at high temperatures. We believe this fact indicates a steric hindrance effect. This deduction is further borne out by the present investigation, because it has been impossible to saponify *iso*-propyl-phenyl-succino-nitril and *isobutyl*-phenyl-succino-nitril further than the half-acid by the usual methods; while *n*-propyl-, ethyl- and methyl-phenyl-succino-nitril are saponified with increasing ease by the usual methods. It should be noted that when the half-nitril half-ester of *isobutyl* or *iso*-propyl-phenyl-succinic acid was saponified, the nitril group remained intact, and from the method of condensation, this nitril group must be adjacent to the phenyl group. The preparation of a compound with an ester group adjacent to the phenyl was attempted by condensing ethyl ester of phenyl-bromo-acetic acid with aliphatic nitrils, but, as yet, positive results have not been obtained. It was hoped that this compound could be prepared so that we might determine, in a measure at least, whether the difficulty of saponification is entirely one of steric hindrance, or both steric hindrance and resistivity of the nitril group to saponification. In this connection Wren and Still<sup>6</sup> say: "The saponification of alpha (racemic) ethyl diphenyl-succinate with aqueous alcoholic potassium hydroxide proceeds normally. . . . ." This would indicate that the character of the nitril group as compared with the ester group entered into the question of saponification. Sulo Kilpi<sup>7</sup> after studying the rate of hydrolysis of aceto-, propiono-, *n*-butyro- and *n*-valero-nitrils with hydrochloric acid and alcohol and aqueous alkali states; "The velocity of hydrolysis increases in the same direction as does the negative character of the carbon atom of the carbonyl group determined according to the system of Michael." Although an accurate determination of the velocity of hydrolysis was not made, it has been definitely shown that the speed and ultimate complete saponification depends upon the character of the alkyl groups introduced. Whether the results are best explained by Michael's system, or on the basis of a steric hindrance effect, we cannot say at the present time. Either theory seems to offer a satisfactory explanation of the observed facts.

### Experimental.

#### Hydrolysis of *Iso*-propyl-phenyl-succino-nitril by the Usual Methods.

(1) Five g. of *isopropyl*-phenyl-succino-nitril was refluxed with a 30% solution of sodium hydroxide for 8 hours. At this time, a portion of the solution was withdrawn (diphenyl-succinonitril) with concentrated hydrochloric acid at 150-160° diphenyl-succinic acid melting at 229-230° was obtained."

Wren and Still (*J. Chem. Soc.*, 107, 445 (1915)) report: "It was further found that the hydrolysis of diphenyl-succinonitril at 200° by means of aqueous hydrochloric acid leads to the formation of meso-diphenyl-succinic acid "

<sup>6</sup> Ref. 5, p. 444.

<sup>7</sup> Kilpi, *Z. physik. Chem.*, 86, 641-81 (1914).

drawn and acidified with hydrochloric acid, whereupon crystals separated. The crystals were dissolved in alcohol and when titrated indicated only a trace of acid. The refluxing was continued for 10 hours, when 0.0526 g. required 1.9 cc. of 0.1 *N* sodium hydroxide for neutralization; calc. for half-acid, 2.4 cc. The mixture was refluxed again for 8 hours, and upon titration indicated the presence of the half-acid. Further refluxing failed to hydrolyze the second nitril group.

(2) Five g. of the nitril was placed in a flask and 100 cc. of 95% alcohol added. Fifteen g. of solid sodium hydroxide was added to the alcohol solution and the whole refluxed for 12 hours. The alcohol was removed by vacuum distillation and the residue acidified with hydrochloric acid just dilute enough to dissolve the ammonium chloride. As in the first case, when the solution was acidified, a crystalline substance separated which, when titrated, showed the presence of one replaceable hydrogen. Further treatment with alcoholic sodium hydroxide gave the same result.

(3) Five g. of the nitril was dissolved in 25 cc. of methyl alcohol and an equal amount of water, to which was added 5 g. of sodium hydroxide. After this solution had been refluxed for 8 hours, 0.1143 g. required 3.2 cc. of 0.1 *N* sodium hydroxide solution for neutralization; calc. for one acid group, 5.13 cc. The refluxing was continued for 30 hours longer, but hydrolysis could not be carried beyond the half-acid stage.

(4) Five g. of the acid was placed in a flask with 100 cc. of conc. hydrochloric acid and the whole refluxed for 2 hours, when the water and acid were evaporated under diminished pressure. The residue was treated again with 100 cc. of conc. hydrochloric acid and refluxed for 8 hours. The crystals which separated from the cold dil. hydrochloric acid solution proved to be the half-acid.

Hydrolysis in every case was best brought about by the use of conc. hydrochloric acid. It was possible to hydrolyze completely the half-ester half-nitril of *n*-propyl-phenyl-, ethyl-phenyl- and methyl-phenyl-succinic acid in 16, 10 and 4 hours, respectively. The half-ester half-nitril of isopropyl-phenyl-succinic acid was hydrolyzed in much the same manner as the nitril and to the same degree. However, the ester group appeared to be more easily hydrolyzed than the corresponding nitril group.

### III. Analysis and Properties of the Acids.

The acids are soluble in alcohol and ether and insoluble in cold water, benzol, petroleum ether, and chloroform. Their solubility in alcohol is a function of the number and relative positions of the carbons of the substituted alkyl groups. Methyl-phenyl-succinic acid is readily soluble in

TABLE I  
ANALYSES, MELTING POINTS AND SOLUBILITIES OF THE ACIDS<sup>a</sup>

Acid	Hydrogen		Carbon		M. p. ° C.	Solubility in 100 g. water at 25° × 10 <sup>3</sup> G.
	Calc. %	Found %	Calc. %	Found %		
isoButyl-phenyl-succinic acid.....	7.02	7.11	67.02	66.84	183.4	13.3
isoPropyl-phenyl-succinic acid.....	6.77	7.05	66.1	66.16	178	20.6
<i>n</i> -Propyl-phenyl-succinic acid.....	6.77	6.87	66.1	66.00	213	2.11
Ethyl-phenyl-succinic acid.....	6.30	6.51	64.86	64.53	196	10.5
Methyl-phenyl-succinic acid.....	5.73	5.89	63.41	63.71	182	41.1

<sup>a</sup> Analyses by F. L. Herman and L. Porter.

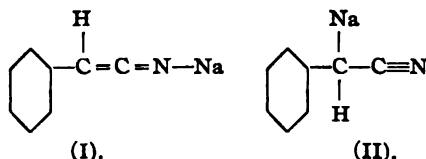
cold methyl or ethyl alcohol and cannot be precipitated from alcohol solutions by the addition of cold water as can the other acids of the series. It can be purified only by recrystallization from hot water. Microscopic examination of the crystals of the acids shows that each one possesses a characteristic crystalline form. The crystals of *isopropyl-phenyl-succinic* acid are especially beautiful.

Four determinations of the molecular weight of *isopropyl-phenyl-succinic* acid were made by the boiling-point method. The molecular weight determined from an average of the four is 241; that calculated, 236.

### Structure of Sodium Benzyl-Cyanide Compound.

During the course of this investigation, a deposit of the sodium compound, formed by sodamide with benzyl cyanide in ether solution, was accidentally allowed to stand on a filter paper. When the ether evaporated auto-oxidation took place accompanied by considerable heat evolution. The heat of the reaction was sufficient to decompose the filter paper completely wherever the residue came in contact with it. It is thought the decomposition of a slight excess of sodamide liberated sufficient heat to start an auto-oxidation. Since such auto-oxidation reactions are in general characteristic of unsaturated compounds, we believe that the results observed indicate a state of unsaturation. The residue left after the reaction was complete was yellow in color with a cork-like texture.

A portion of the product was shaken with water in which it dissolved to give a clear solution. A small amount of the water solution gave a very positive reaction for sodium cyanide. Since the water solution showed no trace of immiscible liquids, such as benzyl cyanide, benzyl alcohol, or benzaldehyde, it was concluded that the remainder of the sodium benzyl-cyanide compound either must have volatilized during the auto-oxidation, or must be present in the residue in a soluble form. A small quantity of the cork-like residue was placed in a distilling flask and heated on an oil-bath. The temperature was raised gradually until as it approached 125° small crystals began to collect on the neck of the flask. The heating was continued until the temperature reached 180°. The crystals were recrystallized from hot water and proved to be benzoic acid. In view of these facts we suggest Formula I for the sodium benzyl cyanide compound,



and we believe the results observed can be explained better by this formula than by Formula II at present current in the literature.

In conclusion the facts seem to indicate that a state of unsaturation

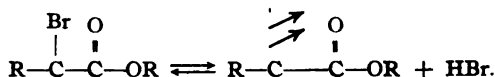
exists in the compound, and since the presence of sodium cyanide and benzoic acid has been shown, this unsaturation must exist between the carbon atoms.

The results and vigorousness of the reaction are probably best explained by (1) assuming that the unsaturation promotes the absorption of oxygen and the cleavage of the compound into benzaldehyde and sodium isocyanide, which always exist in equilibrium with sodium cyanide, cleavage at the ethenoid linkage being a common reaction especially in the presence of alkalis; (2) the fact that benzaldehyde in the presence of air, it is known, readily absorbs oxygen forming benzoyl hydrogen peroxide; and (3) the belief that the peroxide thus formed, being a very active oxidizing agent, interacts with benzaldehyde forming benzoic acid, thus accounting for the vigorousness of the reaction.

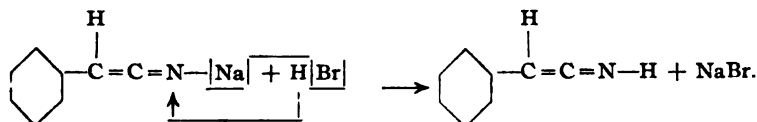
A simple explanation of the condensation reaction on the basis of the iso structure of the sodium benzyl cyanide compound is suggested by Nef's<sup>9</sup> ideas of the aceto-acetic ester and aldol condensations.

The condensation reactions are therefore outlined thus, using the suggested formula.

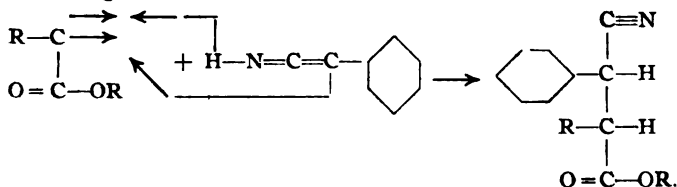
1. The bromo ester dissociates hydrogen bromide.



2. Hydrogen bromide reacts on the sodium benzyl-cyanide giving a ketene-imide structure.



3. The ketene-imide adds to the alkylidene derivative of the ester at the same time undergoing rearrangement as follows.



The work on the structure and properties of other metallic derivatives of benzyl cyanide is being continued.

### Summary.

1. The following new substituted succinic acids were prepared: (1) methyl-phenyl-succinic acid, (2) ethyl-phenyl-succinic acid, (3) *n*-propyl-phenyl-succinic acid, (4) *isobutyl*-phenyl-succinic acid.

<sup>9</sup>Ref. Ann., 298, 218 (1897).



2. The preparation of the acid was brought about by two operations: (1) the condensation of molecules of proper constitution in the molecular proportions to synthesize the desired nitril or ester; (2) the hydrolysis of the nitril or ester.

3. Two methods were used to bring about the condensation: (1) aldehydes of the fatty acid series were converted to the cyanohydrins and condensed with benzyl cyanide by means of sodium ethoxide or sodium methoxide; (2) esters of  $\alpha$ -bromo fatty acids were condensed with benzyl cyanide by means of sodamide.

4. The complete hydrolysis of the nitrils or esters of *isopropyl*- and *isobutyl*-phenyl-succinic acid cannot be brought about by the usual acid or alkali methods, but these substances must be heated in a bomb tube at 130–140° for from 24 to 30 hours. This resistance to hydrolysis is probably due to a steric hindrance effect, to an electrochemical effect of the substituted alkyl group, or to a combination of the two effects.

5. The general properties of each acid vary according to its constitution.

6. A new formula is suggested for the compound formed when sodamide reacts with benzyl cyanide in ether solution.

LINCOLN, NEBRASKA.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF MICHIGAN.]

## DI- $\alpha$ -NAPHTHYL-PHENYL CARBINOL AND DI- $\alpha$ -NAPHTHYL-PHENYL-METHYL.

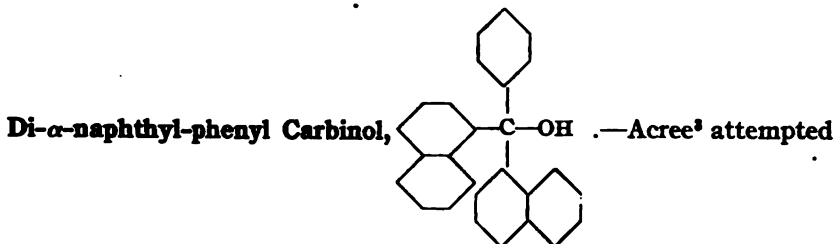
By C. S. SCHOEPPLE.

Received September 6, 1921.

In a previous paper,<sup>1</sup> it has been shown that the hexa-aryl-ethane, di- $\alpha$ -naphthyl-tetraphenyl-ethane, is dissociated to a very marked extent into the free radical,  $\alpha$ -naphthyl-diphenyl-methyl,  $R_3C-CH_2 \rightleftharpoons 2 R_3C$ . This dissociation is influenced by the nature of the solvent, the concentration of the radical in solution, and by the temperature, the latter being the most important factor. Molecular-weight determinations in various solvents freezing at temperatures from 6° to 80°, showed that at 6° the radical exists as 30% dimolecular and 70% monomolecular, the dissociation increasing until at approximately 62° only the monomolecular form is present in solution. However, above this temperature the molecular weight continues to decrease, showing that a further dissociation of the monomolecular form must be taking place, the nature of which could not be ascertained. With the hope of obtaining more information concerning this interesting phenomenon, a study of the free radical di- $\alpha$ -naphthyl-phenyl-methyl was undertaken, since it was known that the naphthyl group exerts a great influence on the extent of the dissociation.<sup>2</sup>

<sup>1</sup> Gomberg and Schoepfle, *THIS JOURNAL*, 41, 1655 (1919).

<sup>2</sup> Gomberg and Schoepfle, *ibid.*, 39, 1672 (1917).



to prepare di- $\alpha$ -naphthyl-phenyl carbinol from benzoyl chloride and  $\alpha$ -naphthyl-magnesium bromide, but found that only  $\alpha$ -naphthyl-phenyl ketone was formed. Elbs<sup>4</sup> obtained the carbinol by heating  $\alpha$ -naphthyl-phenyl- $\beta$ -pinacoline with alcoholic potash, and describes it as a grayish-yellow crystalline crust from ether-alcohol; m. p. 160–170°.

In repeating Acree's experiment, it was found that when benzoyl chloride and  $\alpha$ -naphthyl-magnesium bromide are allowed to react in ether solution, the impure product which is obtained upon decomposition with water and dilute acid consists mainly of  $\alpha$ -naphthyl-phenyl ketone but contains a small amount of di- $\alpha$ -naphthyl-phenyl carbinol which can be isolated only with considerable difficulty. The substitution of ethyl benzoate for benzoyl chloride gives a purer product but, again, the yield of the carbinol is very low, about 10%. When, however, the reaction between ethyl benzoate and  $\alpha$ -naphthyl-magnesium bromide is carried out at a higher temperature, 100–110°, then the yield of the carbinol is increased to about 30–35%. The procedure is as follows. The Grignard reagent is prepared in the usual manner from 10 g. of magnesium and 75 g. of  $\alpha$ -naphthyl bromide in ether. When the reaction is completed, the ether is distilled under reduced pressure, toluene is added, and the flask is immersed in an oil-bath heated to 110–115°. Twenty-five g. of ethyl benzoate is then added slowly to the boiling solution, and after an additional 10–15 minutes' heating, the flask is cooled and the product decomposed with ice and dil. hydrochloric acid. After evaporation of the solvent, the residue is distilled with steam and taken up in benzene, from which the carbinol is obtained in large, colorless crystals containing 1.5 molecules of benzene of crystallization. Yield, about 25 g.

The carbinol is readily soluble in chloroform, carbon disulfide, carbon tetrachloride, ethyl acetate, acetone and ether, fairly soluble in benzene, less soluble in alcohol and acetic acid, and very slightly soluble in petroleum ether. The melting point of the pure carbinol is 166–167°. With conc. sulfuric acid and with perchloric acid, it gives a deep purple color which, however, is transient and soon disappears.

Calc. for  $C_{27}H_{20}O$ : C, 89.96; H, 5.60. Found: C, 89.97, 89.76; H, 5.61, 5.53.

<sup>3</sup> Acree, *Ber.*, 37, 625 (1904).

<sup>4</sup> Elbs, *J. prakt. Chem.*, 35, 507 (1887).

**Additive Compounds with Various Solvents.**—The carbinol forms additive compounds with ether, ethyl acetate, acetone, ethyl alcohol, and benzene. The resulting compound in the case of the first 4 solvents consists of one molecule of the carbinol and one molecule of the solvent; for example,  $C_{27}H_{30}O \cdot C_2H_5OH$ . With benzene, the compound  $2C_{27}H_{30}O \cdot 3C_6H_6$  is formed. These additive compounds are perfectly stable and at room temperature, do not lose the solvent of crystallization even *in vacuo*. They show melting points ranging from 75–100°, at which temperatures the solvent of crystallization is given off.

With chloroform, carbon disulfide, carbon tetrachloride, acetic acid and petroleum ether, no additive compounds are formed.

**Di- $\alpha$ -naphthyl-phenyl-chloromethane and -bromomethane.**—Di- $\alpha$ -naphthyl-phenyl-chloromethane was prepared by treating di- $\alpha$ -naphthyl-phenyl carbinol with acetyl chloride. Ten g. of the carbinol ( $2C_{27}H_{30}O \cdot 3C_6H_6$ ) is dissolved in benzene and 10 g. of acetyl chloride added. After standing for a short time, the solution is concentrated under reduced pressure while the temperature of the solution is kept below 50° to prevent decomposition. Upon the addition of petroleum ether, clusters of colorless crystals are obtained in almost quantitative yield. The material used for the preparation of the free radical was always recrystallized from benzene by the addition of petroleum ether to remove any traces of acid. The chloride is not very stable and slowly becomes colored on standing. It melts at 165–167° with decomposition, and loss of hydrogen chloride.

The chloride was also prepared by passing dry hydrogen chloride into a solution of di- $\alpha$ -naphthyl-phenyl carbinol, but a small amount of the chloride-hydrochloride,  $C_{27}H_{31}Cl \cdot HCl$ , was usually formed. This compound, which has a deep purple color, is unstable and rapidly decomposes to form phenyl-di- $\alpha$ -naphthofluorene. Therefore this method often gives an impure product.

**Analysis.** Calc. for  $C_{27}H_{31}Cl$ : Cl, 9.36. Found: 9.21.

If di- $\alpha$ -naphthyl-phenyl carbinol is treated with acetyl bromide as above, the corresponding di- $\alpha$ -naphthyl-phenyl-bromomethane is obtained in colorless crystals which melt at 125–127° with decomposition, and loss of hydrobromic acid. The bromide, like the chloride, is unstable and becomes colored on standing. It readily forms an additive compound,  $C_{27}H_{31}Br \cdot HBr$ , when treated in solution with hydrogen bromide.

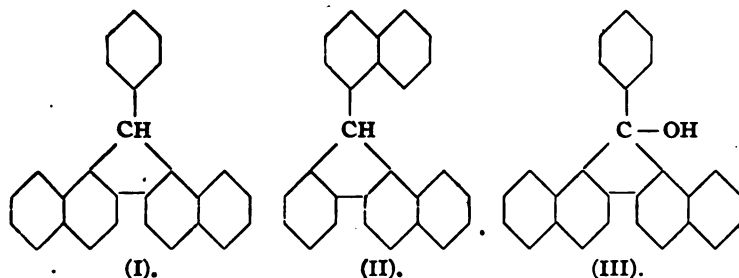
**Analysis.** Calc. for  $C_{27}H_{31}Br$ : Br, 18.88. Found: 18.54.

The chloride and the bromide form additive compounds with mercuric, stannic, ferric, aluminum and zinc chlorides. The additive compounds all have the same deep purple color and all are unstable, decomposing within a short time with the formation of phenyl-di- $\alpha$ -naphthofluorene; consequently, they could not be isolated in pure form.

**Phenyl-di- $\alpha$ -naphthofluorene.**—Phenyl-di- $\alpha$ -naphthofluorene was prepared by boiling an acetic acid solution of di- $\alpha$ -naphthyl-phenyl carbinol. The solution assumes a purple color which soon disappears, and the reaction is completed within a few minutes. The fluorene crystallizes from the acetic acid in fine, colorless needles, the yield being almost quantitative; m. p. 273°. It is fairly soluble in benzene, slightly soluble in ether, and very slightly soluble in acetic acid, in alcohol, and in petroleum ether.

Since naphthyl groups manifest a greater tendency than phenyl groups for the formation of fluorene linkings, it was considered probable that the compound obtained from di- $\alpha$ -naphthyl-phenyl carbinol was phenyl-di- $\alpha$ -naphthofluorene (I), and not the isomeric  $\alpha$ -naphthyl-chrysofluorene (II).

This view was shown to be correct by preparing phenyl-di- $\alpha$ -naphthofluorene from phenyl-di- $\alpha$ -naphthofluorenol as follows.



Phenyl-di- $\alpha$ -naphthofluorenol, III.—Di- $\alpha$ -naphthofluorene,<sup>5</sup> prepared from di- $\alpha$ -naphthyl carbinol, was oxidized to di- $\alpha$ -naphthofluorenone,<sup>6</sup> which upon treatment with phenyl-magnesium bromide gave phenyl-di- $\alpha$ -naphthofluorenol in good yield. One g. of magnesium and 5 g. of bromobenzene in ether are allowed to react and the resulting solution of phenyl-magnesium bromide is added to 2.5 g. of di- $\alpha$ -naphthofluorenone suspended in 250 cc. of dry benzene. After heating this mixture on the water-bath for 2 hours, the product is decomposed with water and dilute acid, and the benzene-ether layer is dried and concentrated. The carbinol is obtained in colorless needles, m. p. 286°. Yield, about 2 g. The carbinol is somewhat soluble in ether and benzene, slightly soluble in acetic acid and alcohol, and very slightly soluble in petroleum ether. With conc. sulfuric acid, it gives a bluish-green color.

*Analysis.* Calc. for  $C_{27}H_{20}O$ : C, 90.47; H, 5.06. Found: C, 90.10; H, 5.10.

The fluorenol is readily reduced by zinc dust and hydrochloric acid in acetic acid solution. 0.5 g. of the fluorenol is dissolved in 100 cc. of acetic acid, 1 g. of zinc dust added, and conc. hydrochloric acid slowly dropped into the boiling solution until a test portion no longer shows a bluish-green coloration with conc. sulfuric acid. A half hour's heating is usually sufficient. The solution is then filtered hot from the excess zinc dust and, as it cools, the phenyl-di- $\alpha$ -naphthofluorene crystallizes in colorless needles. An additional small amount may be obtained by diluting the mother liquid with water and extracting it with benzene. The yield is almost quantitative. The compound is identical with that obtained from di- $\alpha$ -naphthyl-phenyl carbinol and has the same melting point, 273°. Moreover, an intimate mixture of the two compounds showed no change in melting point.

*Analysis.* Calc. for  $C_{27}H_{24}$ : C, 94.70; H, 5.30. Found: C, 94.50, 94.33; H, 5.23, 5.22.

Di- $\alpha$ -naphthyl-phenyl-methane.—Elbs<sup>4</sup> obtained di- $\alpha$ -naphthyl-phenyl-methane by distilling either di- $\alpha$ -naphthyl-phenyl carbinol or  $\alpha$ -naphthyl-phenyl- $\beta$ -pinacolone with zinc dust, and describes it as a grayish-yellow powder when crystallized from ether-alcohol, with an indefinite melting point, about 180°. We prepared this hydrocarbon by reducing the carbinol with zinc dust and acetic acid at a temperature of 75–80°. Two and a half g. of the carbinol is dissolved in 100 cc. of acetic acid and 10 g. of zinc dust is added. The mixture is stirred vigorously and heated at 75° until a test portion is no longer colored by conc. sulfuric acid. From 1 to 2 hours' heating is required. (If during the reduction the temperature rises much above 75°, phenyl-di- $\alpha$ -naphthofluorene is formed.) The solution is then heated to boiling, filtered, and the residue washed with hot acetic acid. The hydrocarbon is precipitated with water, filtered,

<sup>5</sup> Schmidlin and Massini, *Ber.*, 42, 2387 (1909); also Chichibabin and Magidson, *J. prakt. Chem.*, 90, 168 (1914).

<sup>6</sup> Schmidlin and Huber, *Ber.*, 43, 2833 (1910).

dried, and recrystallized from acetic acid or ether. Very fine, colorless needles are obtained. Yield, about 90%; m. p. 204°. It is soluble in benzene, fairly soluble in ether, and very slightly soluble in acetic acid, in alcohol, and in petroleum ether.

*Analyses.* Calc. for  $C_{27}H_{20}$ : C, 94.14; H, 5.86. Found: C, 93.80, 93.66; H., 5.83, 5.86.

**Di- $\alpha$ -naphthyl-phenyl-aminomethane.**—Di- $\alpha$ -naphthyl-phenyl-aminomethane was prepared by passing dry ammonia into a solution of di- $\alpha$ -naphthyl-phenyl-chloromethane or -bromomethane, the latter reacting more readily. Five g. of di- $\alpha$ -naphthyl-phenyl carbinol, dissolved in benzene, is treated with 5 g. of acetyl bromide, and, after standing for 10 to 15 minutes, the solution is thoroughly saturated with dry ammonia. The precipitated ammonium salts are filtered off and the solution is evaporated. Upon addition of ether, the amine is obtained in very fine, colorless crystals. Yield, about 80%. It is soluble in benzene and in chloroform, and but very slightly soluble in ether, in alcohol, and in petroleum ether. The crystals turn brown at about 200° and melt with decomposition at 205–210°, depending on the rate of heating. Upon treatment of the amine with nitrous acid, the carbinol is obtained.

### Di- $\alpha$ -naphthyl-phenyl-methyl.

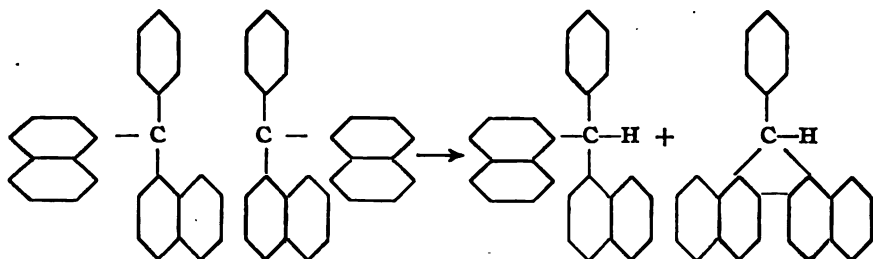
**Preparation.**—Di- $\alpha$ -naphthyl-phenyl-methyl was prepared by shaking a solution of di- $\alpha$ -naphthyl-phenyl-chloromethane with molecular silver in the absence of air. The solution of the free radical has a deep reddish-brown color similar to that of  $\alpha$ -naphthyl-diphenyl-methyl solutions, but more intense. However, the di- $\alpha$ -naphthyl-phenyl-methyl in solution is unstable and the color gradually fades, even when carefully protected from light, until, after a few weeks, it has practically disappeared, although the solution never becomes entirely colorless. All attempts to isolate the free radical in pure form were unsuccessful, although a number of solvents were tried, *e. g.*, benzene, ether, carbon disulfide, and acetone.

**Auto-reduction of the Free Radical.**—Solutions of the free radical which were allowed to stand until decolorized were always found to contain considerable amounts of di- $\alpha$ -naphthyl-phenyl-methane, which would suggest a reaction similar to the auto-reduction of triphenyl-methyl under the influence of light to give triphenyl-methane and di-biphenylene-diphenylethane.<sup>7</sup> Three g. of di- $\alpha$ -naphthyl-phenyl-chloromethane and 3 g. of molecular silver were placed in a 100cc. bottle and enough dry benzene was added almost to fill the bottle, which was then tightly corked. After shaking this mixture for 12 hours, the bottle was allowed to stand for one month protected from the light, by which time almost all of the color of the free radical had disappeared. The silver chloride and excess silver were then filtered off, the benzene evaporated and the residue taken up in ether. Concentration of this solution gave 1.2 g. of di- $\alpha$ -naphthyl-phenyl-methane, and a dark red oil which could not be crystallized.

The same experiment was carried out with ether as the solvent in place of benzene. In this case, phenyl-di- $\alpha$ -naphthofluorene was isolated

<sup>7</sup> Schmidlin and Garcia-Banus, *Ber.*, 45, 1344 (1912).

from the solution, in addition to di- $\alpha$ -naphthyl-phenyl-methane, and the same oily residue was obtained. (The fluorene is less soluble in ether than di- $\alpha$ -naphthyl-phenyl-methane and is the first to crystallize.) This would seem to indicate that part of the free radical in solution reacts as follows.



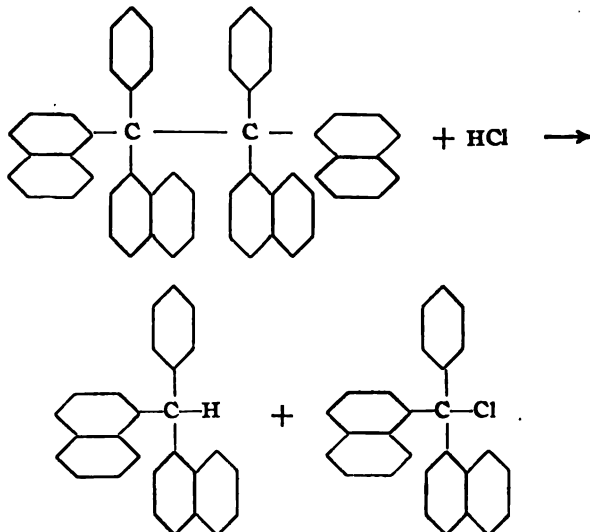
**Action of Oxygen.**—Although a solution of di- $\alpha$ -naphthyl-phenyl-methyl absorbs oxygen and is decolorized, attempts to isolate the corresponding peroxide were unsuccessful. The absorption is rapid at first and the solution becomes practically colorless; then a further gradual absorption takes place for several hours and the solution assumes a dark reddish color. The amount of oxygen absorbed is approximately 150% of that required for the formation of the peroxide, indicating more or less complex decomposition.

One g. of di- $\alpha$ -naphthyl-phenyl-chloromethane in bromobenzene, and 2 g. of molecular silver were sealed in a test-tube and shaken for 12 hours. Upon breaking the tube and exposing to air in the absorption apparatus, which has been described in a previous paper,<sup>8</sup> 47 cc. of oxygen (corrected to standard conditions) was absorbed in the course of 3 hours. The amount required theoretically for the formation of the peroxide is 32.8 cc. When the sample is allowed to stand for any considerable length of time after its preparation, the absorption decreases in proportion to the time which has elapsed but never becomes zero. A sample of the free radical in benzene, prepared by shaking 1.00 g. of the chloride with 2 g. of molecular silver in a sealed tube, was allowed to stand for a month protected from light, by which time the color of the free radical had practically disappeared. Nevertheless, it still absorbed 15 cc. of oxygen in the course of 3 hours. It appears, therefore, that the peroxide and one or more products obtained from the auto-reduction of the free radical are unstable and decompose on exposure to air with the absorption of oxygen.

**Action of Hydrochloric Acid.**—When a solution of di- $\alpha$ -naphthyl-phenyl-methyl is treated with hydrochloric acid in the absence of air, decolorization takes place within a few hours and the resultant colorless

<sup>8</sup> Ref. 2, p. 1661.

solution contains di- $\alpha$ -naphthyl-phenyl-methane and di- $\alpha$ -naphthyl-phenyl-chloromethane.



Consequently, when di- $\alpha$ -naphthyl-phenyl-chloromethane is shaken with excess of molecular silver in benzene which is saturated with gaseous hydrochloric acid, the di- $\alpha$ -naphthyl-phenyl-methyl which is formed immediately reacts with the hydrochloric acid to give the methane and the chloride as above; the latter then reacts with the excess of molecular silver to form more of the free radical and so on to completion. Two and a half g. of chloride and 5 g. of molecular silver were shaken in benzene saturated with hydrochloric acid. About 10–12 hours was required for the complete disappearance of the color of the free radical. Two and a tenth g. of di- $\alpha$ -naphthyl-phenyl-methane (92.5% yield) was obtained upon concentrating the benzene solution and adding petroleum ether. No other compounds could be isolated from the solution.

### Summary.

1. Di- $\alpha$ -naphthyl-phenyl carbinol and the corresponding chloride, bromide, amine, methane, fluorene, and fluoreneol have been synthesized and described.

2. Di- $\alpha$ -naphthyl-phenyl-methyl has been prepared in solution and found to be unstable. The auto-reduction, and the action of oxygen and of hydrochloric acid upon the free radical are discussed.

ANN ARBOR, MICHIGAN.

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF COLUMBIA UNIVERSITY, No. 382.]

## THE ISO-ELECTRIC POINT OF COLLAGEN.<sup>1</sup>

BY ARTHUR W. THOMAS AND MARGARET W. KELLY.

Received September 17, 1921.

In 1910, Michaelis and Mostynski<sup>2</sup> published their theory of the iso-electric point of a protein, defining it as that reaction where the relation of the concentration of the hydrogen ions to hydroxyl ions in the solution is the same as the relation of the acid dissociation constant ( $k_a$ ) of the protein to its basic dissociation constant ( $k_b$ ). At the iso-electric point the number of protein anions is equal to the number of protein cations present and the sum of the protein ions in relation to non-ionized protein is at its minimum.

Previous to 1910, Michaelis tried to determine the sign of the electrical charge of proteins in solution by U-tube electrophoresis, and noted that the migration of a particular protein was cathodic or anodic depending entirely upon the reaction of the solution. These experiments led to the derivation of the theory of the iso-electric point, and several papers since, by Michaelis and co-workers, give values for the iso-electric points of several proteins.

Prior to Michaelis' researches, proteins were considered merely as colloids, and explanation of their behavior in aqueous solutions, in the presence of electrolytes, was influenced by the supposed fundamental effect of the Hofmeister ion series, selective adsorption, etc. The tenacity with which this point of view has held even up to date ignoring the amphoteric properties of proteins has been an obstacle in the progress of the physical chemistry of the proteins.

The recent brilliant work by Jacques Loeb<sup>3</sup> has most strikingly shown the great importance of a knowledge of the iso-electric points of proteins. Loeb clearly demonstrated in the case of gelatin, albumin, and casein that at the iso-electric points these proteins are in the most inert condition, while on the acid side they exist and react as cations, and on the alkaline side they are anions.

The making of leather consists fundamentally in converting the sclero-proteins, or albuminoids of hide substance into an insoluble and impu-trescible substance. This consists generally in combining the protein with the complex weakly acidic substances known as tannins, or in converting it to a chromium compound. Obviously, a better understanding of these reactions requires a knowledge of the iso-electric point of hide protein, or collagen.

<sup>1</sup> Presented before the Leather Chemistry Section at the 62nd Meeting of the American Chemical Society, New York City, Sept. 6-10, 1921.

<sup>2</sup> Michaelis and Mostynski, *Biochem. Z.*, 24, 79 (1910).

<sup>3</sup> Series of papers in *J. Gen. Physiol.*, 1918-21.



This investigation was undertaken with the purpose of establishing the iso-electric point of hide substance, *i. e.*, that hydrogen-ion concentration of the solution in which hide substance protein is in its minimum ionized state, on the alkaline side of which it exists as an anion, and on the acid side as a cation.

Since it has been most clearly proved by Loeb that a protein is at its minimum degree of swelling at the iso-electric point, we decided to try to locate the point by swelling measurements.

### Swelling Method.

In all swelling experiments, 1920 American Standard Hide Powder<sup>4</sup> was used as source of hide substance. Since hide substance is insoluble in water, the simple swelling technique as used by Loeb was not applicable to this substance. Some method had to be devised whereby the interstices between the particles could be reduced to a minimum. This was accomplished by sifting the hide powder through a 20-mesh sieve, and centrifuging the fine siftings in contact with solutions of various hydrogen-ion concentrations as described below.

Portions of 0.3 g. each of fine siftings were placed in each of a series of eight 100cc. "oil tubes" (graduated tubes drawn out to a conical end), in which there had been previously placed 50 cc. of solution, and carefully shaken. When the hide powder had become thoroughly wetted, another 50 cc. of solution was added and the tubes were allowed to stand

### EXPERIMENT 8

Approx. molar conc. of solution			Log. CH +	Volume of hide powder after standing in contact with solution for the stated time					
				Hours	24 Cc.	48 Cc.	72 Cc.	96 Cc.	384 Cc.
1	0.0002	HCl	.....		2.7	2.8	2.7	2.5	2.7
2	0.0001	HCl	- 3.75		2.3	2.5	2.4	2.3	2.4
3	Dist. H <sub>2</sub> O		- 5.58		2.1	2.3	2.2	2.1	2.3
4	Dist. H <sub>2</sub> O		- 5.58		2.1	2.1	2.3	2.1	2.3
5	0.0001	NaOH	- 9.18		2.1	2.4	2.5	2.8	3.0
6	0.0001	NaOH	- 9.18		2.1	2.3	2.6	2.7	2.8
7	0.00025	NaOH	-10.00		2.4	3.0	3.2	3.4	3.5
8	0.0005	NaOH	.....		3.0	3.4	3.5	3.5	3.7

### HYDROGEN-ION CONCENTRATION OF WASHINGS

Solution	Washings after the stated time		
	Hours 24	72	96
3	-5.25	-5.58	-5.88
4	-5.43	-5.88	-5.88
5	-5.88	-6.45	-6.64
6	-5.88	-6.45	-6.64

<sup>4</sup> Manufactured by the Standard Mfg. Co., Ridgway, Pa.

for 24 hours. They were then centrifuged altogether for 5 minutes at about 2000 r. p. m., and the volumes occupied by the various hide-powder specimens recorded. The supernatant liquid was poured off, and an additional 100 cc. of solution added, the contents thoroughly mixed, allowed to stand for an additional 24 hours, and the centrifuging, etc., repeated. An example of such an experiment precedes.

It will be seen that upon 24 hours contact with the solutions, the minimum swelling is indicated in distilled water and in 0.0001 *M* sodium hydroxide, but upon repeated treatment, the 0.0001 *M* sodium hydroxide solutions show a slightly greater swelling than distilled water, thus according to this technique, setting the distilled water as the solution nearest the hydrogen-ion concentration of the iso-electric condition of the hide substance, namely  $\log C_{H^+} = -5.58$ . It is noted that after 24 hours contact with hide substance, the logarithm of the hydrogen-ion concentration of the distilled water washings became lower, from  $-5.58$  to  $-5.88$ , which may be explained as due to removal of carbonic acid by the hide protein. The 384-hour tubes were discarded on account of putrefaction having taken place to a small extent.

In a subsequent experiment a few drops of toluol were added to each tube. Instead of letting the tubes containing the hide powder stand for 24 hours in contact with the solutions, they were rotated in a tumbling machine for 1 hour to insure thorough mixing, and then centrifuged for 5 minutes, the volumes read, washings decanted, and the operation repeated several times, but it is evident that differences between the tubes of minimum swelling and tubes containing solutions beyond the minimum swelling point were not of any significant magnitude. There was a large error involved in reading the volumes of the hide powders because of uneven settling, and although the technique indicated that the hide powder in contact with distilled water was nearest the iso-electric point, this point was by no means definitely established. The addition of toluol made the readings more doubtful because some of the powder was adsorbed by the toluol layer and thus removed from the bulk of the deposit in the conical bottom of the tube, and in addition a small part of the powder stuck to the side of the tube.

The swelling method for this particular protein is, therefore, applicable only for the purpose of locating the approximate iso-electric region when solutions of widely differing hydrogen-ion concentrations are employed and consequently large swelling differences are obtained. The method, even for approximate results, must involve continued washing or treatment with the solutions until the hydrogen-ion concentration of the washings is identical with that of the original solutions, thereby insuring that equilibrium has been reached and all impurities removed in each case.

The method is slow and laborious, and since the addition of toluol is detrimental, it is not easy to reach equilibrium before decomposition sets in.

For these reasons it was decided to employ the dye technique. As Loeb has shown that protein can combine with cations only on the alkaline side of the iso-electric point, and with anions only on the acid side, collagen should combine with the colored cation of a basic dye when on the alkaline side and with the colored anion of an acid dye on the acid side of its iso-electric point.

### Dye Method.

In these experiments, 4 different batches of hide powder were employed, —1921, 1920 and 1919 (kindly furnished by Dr. L. E. Levi), and 1918 (kindly furnished by Mr. G. W. Schultz).

The acid dye used throughout was Martius yellow, and fuchsin served as basic dye, except in one case where neutral red was employed.

**First Technique.**—Six 1g. portions of hide-powder siftings were placed in 250cc. beakers, and 100 cc. of solutions of various concentrations of hydrogen ion were added. The mixtures were frequently stirred, and at the end of 18 hours were filtered through small pads of cotton on Gooch funnels and washed several times with a new portion of the original solutions. Finally they were treated with distilled water 2 or 3 times. A 20cc. portion of a 0.001% solution of the basic dye, or a 0.002% solution of the acid dye was poured on the residue on each funnel and allowed to drain through. The solutions of fuchsin were completely decolorized where the hide powder was decidedly on the alkaline side of its iso-electric point, and the Martius yellow solutions decolorized by the hide powder which was definitely acid. In such instances more dye was poured through. In our early experiments the residues were then washed with distilled water until all uncombined dye had been removed, but later were washed with solutions of the same hydrogen-ion concentration as those in which the hide powders had been soaked in order to preclude any chances of hydrolysis of the protein-dye compound.

The residues were then examined for color and those two samples of hide powder (both soaked in solutions of the same hydrogen-ion concentration) which showed minimum fixation of color were judged to be in the iso-electric condition.

Possibly an explanation is required at this point because of the popular assumption that at the iso-electric point a protein is absolutely inert and in an un-ionized state. Relatively speaking this is correct, but in an absolute sense it is not. Actually a protein is at its minimum degree of ionization at the iso-electric point and is capable of combining with either a cation or an anion to a slight degree. This point has been discussed by Sørensen.<sup>5</sup>

This technique indicated that the iso-electric point is in the region of log  $C_{H^+}$   $-5.25$  to  $-6.45$ ; but it was found faulty as pointed out in the swelling experiments, since the hide powder was treated only once with the contact solutions.

**Second Technique.**—The portions of hide powder and solutions were placed in 400cc. bottles fitted with rubber stoppers and rotated for one hour in a tumbling machine.

<sup>5</sup> Sørensen, *Compt. rend. trav. lab. Carlsberg*, 12, (1915-17).

In the first experiments (a) with this technique no test for equilibrium was applied but later (b) the supernatant solutions were tested for hydrogen-ion concentration, new portions of solutions placed on the protein in the bottles and tumbled for another hour, etc., until the decanted solutions showed the same hydrogen-ion concentration as the originals. Twenty cc. portions of dye solutions were added and the contents tumbled for 10 minutes when the contents were poured through glass-wool pads in Gooch funnels. They were then washed with solutions of the same hydrogen-ion concentration as those in which they had been soaked.

**Third, Technique.**—The whole operation was carried out in "oil tubes" instead of using bottles. The advantages of this operation were that at the end of each washing, the powder was packed down by centrifuging before the liquid was poured off, and instead of a diffuse layer of treated hide powder in Gooch funnels, the color or lack of color was more easily distinguishable in the columns of powder in the apices of the tubes.

The results of these experiments are summarized below. For economy of space the details of each experiment are omitted, and only Nos. 10, 19 and 20 are given as typical.

#### EXPERIMENT 10

Portions of 0.5 g. of 1920 hide-powder siftings treated in bottles successively with 200, 100, 100 and 100 cc. of solution (2nd technique (a))

Approx. molar conc. of solution		Color after washing		Log $\text{CH}^+$ of solution
		Fuchsin	Martius yellow	
0.0001	HCl	faint pink <sup>a</sup>	yellow	-3.8
0.000075		faint pink	yellow	-4.0
0.00005		pale pink	pale yellow	-4.6
0.000025		pale pink	colorless	-4.9
Dist. $\text{H}_2\text{O}$		deep pink	colorless	-5.6
0.000025	NaOH	deep pink	colorless	-6.1

\* These hide powders always retained a faint trace of the fuchsin and for this reason neutral red was substituted in Expt. No. 20.

The iso-electric point is indicated at -4.6, or possibly between -4.6 and -4.9.

#### EXPERIMENT 19

Each bottle containing 0.5 g. of siftings from 1918 hide powder treated as described in Technique 2 (b)

Approx. molar conc. of solution		Color after washing		Log. $\text{CH}^+$ of solution
		Fuchsin	Martius yellow	
0.00006	HCl	faint pink	yellow	-4.1
0.00004				-4.2
0.00003				-4.6
0.00002		pale pink	colorless	-4.8
0.00001				-5.4
Dist. $\text{H}_2\text{O}$		pink	colorless	-5.8

The above experiment would indicate that the iso-electric point is -4.8 to -5.4, or -5.1.

#### EXPERIMENT 20

Each bottle containing 0.5 g. of siftings from 1918 hide powder, treated by Technique 2(b). Instead of adding 20 cc. of very dilute dye solution, 8 drops of 0.1%

neutral red were added to one set of samples during the last treatment with solution, and 16 drops of 0.1% Martius yellow to a corresponding set of samples.

Approx. molar concn. of solution		Color after washing	Log $\text{CH}^+$ of solution	
		Neutral red	Martius yellow	
0.0001	HCl	colorless	.....	-3.8
0.00006			.....	-4.0
0.00004			.....	-4.2
0.00003			yellow	-4.6
0.00002			pale yellow	-4.8
0.00001			colorless	-5.2
Dist. $\text{H}_2\text{O}$		pale pink	colorless	-5.4
0.0001 NaOH		pale pink	.....	-6.0

The iso-electric point is indicated at -4.8 to -5.4, or -5.1.

#### SUMMARY OF DYE TECHNIQUE EXPERIMENTS

Expt.	Material	Method	Iso-electric $\text{C}_\text{H}^+$	Remarks
10	0.5 g. of 1920 H. P. siftings in 400cc. bottles	2nd tech. (b) 4 treatments	-4.6	Equilibrium reached as shown by $\text{C}_\text{H}^+$ of washings.
11	1921 siftings as in No. 10	2nd tech. (b) 6 treatments	-4.5	
12	1920 siftings as in No. 10		-4.5 to -4.6	
13	1921 siftings as in No. 10		-4.1?	
14	1920 siftings, 0.15 g. in 15 cc. oil tubes	3rd technique 16 treatments	-4.2 to -5.0	
15	0.3 g. of 1921 siftings in 100cc. tubes	3rd technique 4 treatments	-4.2 to -5.0	
16	0.3 g. of 1920 siftings	3rd technique 9 treatments	-4.2 to -4.8	
17	0.3 g. of 1919 siftings	3rd technique 11 treatments	-4.6 to -5.3	
18	0.5 g. of 1919 siftings	2nd tech. (b)	-4.7 to -5.6	
19	0.5 g. of 1918 siftings		-4.8 to -5.4	
20	0.5 g. of 1921 siftings		-4.8 to -5.4	

Inspection of these results reveals a failure to obtain a sharp iso-electric point for hide substance after many experiments. We conclude, therefore, that hide substance, generally referred to as collagen, is a mixture of proteins rather than one simple protein and possibly the differences in properties noticed in the tanning of skins from different animals may be due to the different distribution of the proteins in the hide substance.

The iso-electric point of the proteins of hide substance is at hydrogen-ion concentration  $10^{-5}$ , as determined by means of American Standard Hide Powder.

At various times the iso-electric points of several proteins have been reported in the literature, and since they are not available in any one place, we append them hereto.

We take pleasure in expressing our indebtedness to Messrs. A. F. Gallun and Sons Company of Milwaukee, Wisconsin, for their generous support of this investigation.

		Reference
Casein (cow).....	2.4-2.5 $\times 10^{-5}$	6
	1.8 $\times 10^{-5}$	7
	2 $\times 10^{-5}$	8
Gelatin.....	2.5 $\times 10^{-5}$	9
	2 $\times 10^{-5}$	10
Serum albumin.....	2 $\times 10^{-5}$	11
Serum globulin.....	3.6 $\times 10^{-6}$	7
Egg albumin (hen).....	1.5 $\times 10^{-5}$	12
Denatured serum albumin.....	0.4 $\times 10^{-5}$	11
Oxyhemoglobin.....	1.8 $\times 10^{-7}$	14
Carbon monoxide hemoglobin.....	1.7 $\times 10^{-7}$	15
Reduced hemoglobin.....	1.7 $\times 10^{-7}$	15
Stroma globulins of blood corpuscles.....	1 $\times 10^{-5}$	13, 14
Red blood cells.....	2.5 $\times 10^{-5}$	16
Yeast extract protein (globulin).....	2.5 $\times 10^{-5}$	21
Gliadin.....	6.0 $\times 10^{-10}$	7
Edestin.....	1.3 $\times 10^{-7}$	7
Tuberin (potato).....	approx. $10^{-4}$	17
Carrot protein.....	approx. $10^{-4}$	17
Tomato protein.....	approx. $10^{-5}$	17
Trypsin.....	1.35-2.6 $\times 10^{-4}$	18
Pepsin.....	5.5 $\times 10^{-3}$	19
Nucleic acid.....	approx. 2 $\times 10^{-1}$	20

## NEW YORK CITY.

- <sup>6</sup> Michaelis and Pechstein, *Biochem. Z.*, 47, 260 (1914).  
<sup>7</sup> Rona and Michaelis, *ibid.*, 28, 193 (1910).  
<sup>8</sup> Loeb, *J. Gen. Physiol.*, 2, 577 (1920).  
<sup>9</sup> Michaelis and Grineff, *Biochem. Z.*, 41, 373 (1912).  
<sup>10</sup> Loeb, *J. Gen. Physiol.*, 1, 39 (1918).  
<sup>11</sup> Michaelis and Davidsohn, *Biochem. Z.*, 33, 456 (1911).  
<sup>12</sup> Sørensen, Ref. 5.  
<sup>13</sup> Michaelis and Davidsohn, *Biochem. Z.*, 41, 102 (1912).  
<sup>14</sup> Michaelis and Takahashi, *ibid.*, 29, 439 (1910).  
<sup>15</sup> Michaelis and Bien, *ibid.*, 67, 198 (1914).  
<sup>16</sup> Coulter, *J. Gen. Physiol.*, 3, 309 (1921).  
<sup>17</sup> Cohn, Gross and Johnson, *ibid.*, 2, 145 (1919).  
<sup>18</sup> Michaelis and Davidsohn, *Biochem. Z.*, 30, 481 (1911).  
<sup>19</sup> Michaelis and Davidsohn, *ibid.*, 28, 1 (1910).  
<sup>20</sup> Michaelis and Davidsohn, *ibid.*, 39, 496 (1912).  
<sup>21</sup> Fodor, *Kolloid. Z.*, 27, 58 (1920).

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF JOHNS HOPKINS UNIVERSITY.]

## THE TRANSFER OF HYDROGEN FROM AN ALCOHOL TO AN ALDEHYDE.

BY C. H. MILLIGAN AND E. EMMET REID.

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## Historical.

Since it has become known that, in presence of certain catalysts, alcohols and hydro-aromatic compounds set free hydrogen, and that certain other compounds are hydrogenated under similar conditions, a number of efforts have been made to combine the two processes, utilizing the hydrogen liberated in the one to supply the hydrogen required by the other. If this can be accomplished, many difficulties which are met with in the manufacture of pure hydrogen are avoided and, if the substance which gives up its hydrogen is worth more for the loss, as is the case when ethyl alcohol passes into the more valuable acetaldehyde, the cost of the hydrogen is eliminated.

The ideal case is one in which the dehydrogenation of the one substance and the hydrogenation of the other take place with the same catalyst and at the same temperature.

For the reaction to go, the energy change must be in the right direction, as a catalyst cannot be expected to push anything up hill.

Both of these conditions are fulfilled in the case studied by Zelinski and Glinka<sup>1</sup> who treated methyl tetrahydro-terephthalate with palladium and obtained the terephthalate and the hexahydro-terephthalate, one portion of the tetrahydro- giving off hydrogen which was taken up by the other. In this case the energy change is in the right direction since the partially hydrogenated benzene ring is less stable than the fully hydrogenated or the unhydrogenated.

Bösesken<sup>2</sup> has studied a similar case. He passed dihydro-benzene, and also tetrahydro-benzene, over nickel at 180°, and he sealed up the latter hydrocarbon with palladium for some time. In all cases a mixture of benzene and cyclohexane was obtained. He gives as the heat of combustion of dihydro-benzene 847.5 Cal. and that of a mixture of  $\frac{1}{3}$  benzene and  $\frac{2}{3}$  cyclohexane 832.5 Cal., the difference being 15.0 Cal. The reaction went as was expected.

Meyer and Eckert<sup>3</sup> mention the dehydrogenation of ethyl alcohol to acetaldehyde and the addition of the hydrogen to benzoquinone or thymoquinone with the formation of the corresponding quinols, under the influence of light.

Armstrong and Hilditch<sup>4</sup> transformed a mixture of cyclohexanol by the action of nickel into cyclohexanone and methyl phenylpropionate.

Padóe and Foresti<sup>5</sup> made a quantitative study of the transfer of hydrogen from iso-propyl alcohol to diethyl ketone and to benzene, with the formation of diethyl

<sup>1</sup> Zelinski and Glinka, *Ber.*, **44**, 2305 (1911).<sup>2</sup> Bösesken, *Rec. trav. chim.*, **37**, 255 (1918).<sup>3</sup> Meyer and Eckert, *Monatsh.*, **39**, 241 (1918).<sup>4</sup> Armstrong and Hilditch, *Proc. Roy. Soc.*, **96A**, 322 (1917).<sup>5</sup> Padóe and Foresti, *Atti. accad. Lincei*, **23**, II, 84 (1914).

carbinol and cyclohexane, respectively. They found equilibria corresponding to those calculated from the Nernst heat theorem.

Sabatier and Murat<sup>6</sup> passed the vapors of alcohols with benzaldehyde, benzophenone, benzyl alcohol and acetophenone over thoria at 420° and got complete reduction to toluene, ethylbenzene and diphenyl methane.

Kayser<sup>7</sup> has patented the hydrogenation of unsaturated oils by heating them with borneol or *iso*-borneol in the presence of nickel.

### The Present Investigation.

In our study we have used ethyl alcohol with heptaldehyde, benzaldehyde, phenyl-acetaldehyde and citronellal over ceria at 300–380° and have obtained the corresponding alcohols along with acetaldehyde. The transformation is never complete. There is considerable condensation of the aldehydes to gummy products which foul the catalyst in a short time and stop the transformation. The catalyst may be regenerated by treatment with steam followed by oxides of nitrogen and a second treatment with steam. A small proportion of manganese in the ceria appears to increase its activity. On account of the destruction of a part of the aldehyde, the amount of alcohol that can be recovered from the product is much less than the amount of aldehyde that has disappeared. A small amount of benzyl benzoate was found in the product when benzaldehyde was used.

With copper on an inert support we have obtained results similar to those of Sabatier and Murat with thoria, but at a lower temperature, 330–360°; that is, benzaldehyde is reduced all the way to toluene.

Ethyl alcohol was chosen rather than methyl on account of the greater difference between its heat of combustion and that of its aldehyde which gives a greater driving force to the reaction.

### Experimental.

**Ceria Catalyst.**—To a solution of 30 g. of cerium nitrate in 80 cc. of water, 10 g. of fluffy asbestos was added, care being taken to prevent packing. The beaker containing this mixture was placed in an evacuated desiccator over sulfuric acid till the water had evaporated, leaving a porous mass which was cut into pieces and packed in the catalyst tube where it was heated slowly up to 180° in a current of air. Alcohol vapors were passed through the tube till the nitrate was decomposed and then steam to remove all volatile matter.

A catalyst prepared in this manner showed considerably greater activity in esterification than one prepared in the usual way by decomposing the nitrate by heat alone at 270° to 350°. With an equimolar mixture of acetic acid and ethyl alcohol with 110 cc. of vapor per minute at 250°,

<sup>6</sup> Sabatier and Murat, *Compt. rend.*, 157, 1499 (1913); *Bull. soc. chim.*, [4] 15, 227 (1914).

<sup>7</sup> Kayser, U. S. pat. 1,134,746; *C. A.*, 9, 1401 (1916).



64% and 42%, respectively, of esterification were obtained with the two preparations of ceria.

**Apparatus and Methods.**—We have used 12 g. of ceria suspended on 9 g. of asbestos in a Pyrex glass tube, the free space in the tube being estimated at 93 cc. This tube was heated in an electric tube furnace automatically regulated to  $\pm 1^\circ$ .

The aldehyde was mixed with 2 to 3 equivalents of ethyl alcohol, allowed to drop at the desired rate into a heated space and the vapors were passed into the catalyst tube. The volume of vapors passing through the tube was calculated from the number of drops per minute, from the weight of a known number of drops from the same tip, and from the temperature, etc.

The condensate from the furnace was distilled till the boiling point was reached,  $100^\circ$  to  $120^\circ$ , and the aldehyde determined in the residue. A blank on known mixtures gave results about 10% low when treated in the same way, hence 10% was added to the amount of aldehyde found.

The aldehyde in the product was estimated by a modification of the method of Seyewetz and Bardin<sup>a</sup> as described by Kingscott and Knight.<sup>b</sup> About 0.5 g. of the sample was treated with 10 cc. of a 20% solution of sodium sulfite made neutral to phenolphthalein, and the alkali set free was titrated slowly with 0.2 *N* acetic acid. Vigorous shaking was necessary to complete the reaction in reasonable time, about 25 minutes being required for a titration. The addition of alcohol hastens the reaction but obscures the end-point. This method gives constant results with simple aldehydes, though somewhat low. We obtained the following results on known samples: with pure heptaldehyde, 98.8, 99.0 and 98.1%; with benzaldehyde, 97.5%; with cinnamic aldehyde, 94.0 and 93.7%; with commercial citronellal, 90.5 and 90.5%; with citral, 90.2, 91.0 and 90.5%. Since citral combines with two molecules of bisulfite the titrations with it have to be divided by 2.

**Results.**—Phenylacetaldehyde at  $330^\circ$  passed at the rate of 220 cc. of vapor per minute gave 20% of phenylethyl alcohol. Benzaldehyde gave rather less than 20%.

Cinnamic aldehyde and citral gave none of the corresponding alcohols.

The largest amount of study was put on heptaldehyde. The aldehyde was prepared by destructive distillation of castor oil and carefully purified by fractionation in a vacuum. The amount of aldehyde disappearing when heptaldehyde with 3 moles of ethyl alcohol is passed over ceria at various temperatures is given in tabular form.

<sup>a</sup> Seyewetz and Bardin, *Bull. soc. chim.*, [3] 33, 1000 (1905).

<sup>b</sup> Kingscott and Knight, "Methods of Organic Analysis," Longmans, Green, and Co., 1914, p. 245.

Rate per min. Cc.	Aldehyde disappearing at		
	330° %	350° %	370° %
96	76	100	95
144	76	79	83
238	70	71	77
357	61	63	78
475	45	58	72
640	..	..	73

From 60 g. of the product, collected from several runs, 15 g. of hexyl alcohol was isolated.

With citronellal, the temperature must be kept close to 315° as at higher temperatures the formation of condensation products is excessive and at lower the reaction is too slow. A mixture of 12 g. of citronellal and 10 g. of ethyl alcohol was passed over the ceria at 315° at the rate of 250 cc. of vapors per minute. The product was fractionated and the portion boiling from 180° to 230° was heated with 8 g. of phthalic anhydride for 3 hours at 100°. The monophthalic ester was dissolved in 50 cc. of 10% sodium carbonate solution and extracted several times with ether to remove non-alcohols. The ester was saponified by sodium hydroxide and the citronellal distilled with steam, yielding 6 g. or about 50%. At 300° and at 320° much smaller yields were obtained.

**Sealed Tube Experiments.**—A mixture of 30 g. of citronellal and 15 g. of absolute ethyl alcohol was heated in a sealed glass tube with 3 g. of the ceria-asbestos catalyst for 12 hours at 220°. After fractionation the high-boiling portion was put through the phthalic anhydride treatment and yielded 9 g. of alcohol, apparently citronellol. This was repeated, heating to 195° for 14 hours, and 12 g. of the alcohol obtained.

### Summary.

By passing the vapors of aldehydes mixed with ethyl alcohol over ceria at 300–380° the aldehyde is hydrogenated to the corresponding alcohol and the ethyl alcohol is dehydrogenated to acetaldehyde. Benzyl, phenyl, ethyl and heptyl alcohols and citronellol have been thus prepared. The yields are low and the life of the catalyst is short on account of fouling, probably due to condensations of the aldehydes.

BALTIMORE, MARYLAND.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF JOHNS HOPKINS UNIVERSITY.]

## THE ETHYLATION OF BENZENE AND NAPHTHALENE.

BY C. H. MILLIGAN AND E. EMMETT REID.

Received October 6, 1921.

It has long been known that benzene may be ethylated to form ethylbenzene, di-ethyl-, triethyl-, etc., even up to hexa-ethylbenzene when it is treated with ethyl chloride in the presence of aluminum chloride according to the Friedel and Crafts reaction.

Balsohn<sup>1</sup> substituted a mixture of ethylene and hydrogen chloride for ethyl chloride, assuming that the two would unite to form ethyl chloride which would then react. As hydrogen chloride is regenerated in the reaction, very little of it need be present. In fact Balsohn found that the preparation could be carried out without the addition of any hydrogen chloride; apparently aluminum chloride in the presence of traces of water, etc., furnished sufficient hydrogen chloride to keep the reaction going.

He used 400 g. of benzene with 50 g. of aluminum chloride and passed ethylene into the mixture for "several days" at 70° to 90°, thus obtaining 170 g. of ethylbenzene, 135 g. of di-, 75 g. of tri-ethyl benzene and 20 g. of higher-boiling products. From these figures it appears that about 154 g. of ethylene had been taken up. As he passed in 280 g. of ethylene, only 55% of it was absorbed.

Under the conditions described by Balsohn, this preparation is tedious as to time and wasteful of material, and as a matter of fact does not seem to have come into general use.

## The Present Investigation.

It seemed to us likely that efficient stirring might so increase the contact of the ethylene with the aluminum chloride and benzene that this would become a practical method of ethylating benzene and its homologs. Experiment has verified this prediction.

According to McDaniel,<sup>2</sup> benzene dissolves 3 volumes of ethylene at 22°, 2.5 volumes at 50° and probably not over 2 volumes at 80°. The dissolved ethylene may react ever so rapidly, but the formation of the product will be slow unless the solution is re-saturated quickly.

With high-speed stirring it has been found possible to cause benzene containing aluminum chloride to react with 8 volumes of ethylene per minute, the ethylene being totally absorbed so that ethyl benzene and its higher ethylated homologs become readily available. We have used a rapidly rotating metal stirrer of the Witt<sup>3</sup> type. The horizontal cross piece is replaced by a disc 37 mm. in diameter by 4 mm. thick with eight

<sup>1</sup> Balsohn, *Bull. soc. chim.*, [2] 31, 539 (1879).

<sup>2</sup> McDaniel, *J. Phys. Chem.*, 15, 605 (1911).

<sup>3</sup> Witt, *Ber.*, 26, 1696 (1893).

## ETHYLATION OF BENZENE AND NAPHTHALENE.

2mm. radial holes which open into a central cavity. The lower vertic portion was replaced by a bell-shaped extension about 15 mm. in diameter and extending downward about 5 mm. The ethylene was delivered by a tube which terminated just below this bell so that the bubbles were drawn through the stirrer and broken up by its rapid rotation.

The stirrer was run at ten to twelve thousand r. p. m. For large scale operations a stirrer of the type proposed by Thoens<sup>4</sup> or by Ittner<sup>5</sup> would doubtless be more efficient.

The reaction is best carried on at 70–90°. With efficient stirring the absorption of the ethylene is extremely rapid after an incubation period till about 4 moles of ethylene are absorbed for 1 of benzene, and decreases thereafter.

The ethylene is purified and dried by passing it through towers or wash-bottles filled with suitable materials. It is passed in at such a rate that it is almost totally absorbed. If too much gas is delivered, hydrogen chloride is carried out and the reaction slows, in which case the original speed may be restored by passing in some hydrogen chloride.

It is not possible to conduct the reaction so as to form a single product since some di-ethyl-benzene is formed even before all of the benzene is attacked, but when 1 mole of ethylene is used to 1 of benzene, as in Expt. 3 below, more than half of the product is mono-ethyl-benzene. In Expt. 4, 7.4 moles of ethylene were absorbed by 2.5 of benzene and 272 g., or 1.67 moles of tri-ethyl-benzene obtained, accounting for 5 out of 7.4 moles of ethylene added.

After the reaction is run for a time, if the mixture is cooled it separates sharply into layers, the upper, practically clear and very liquid, the lower, dark and viscous. It is best to work up the two layers separately. The upper layer contains only a trace of aluminum chloride and consists of unchanged benzene with the lower ethylation products and relatively small amounts of the higher. The liquid is shaken with acidulated water, dried and fractioned. The lower layer, which is much the smaller, contains practically all of the aluminum chloride associated with higher ethylated benzenes, particularly penta-ethyl-benzene. It may be worked up by pouring upon ice and hydrochloric acid; it is then washed, dried and fractionated under reduced pressure in the case of the high-boiling portion.

The hexa-ethyl-benzene fraction solidifies and is centrifuged and washed with a little alcohol. It is readily obtained as a snow-white solid. The highest fractions contain a fluorescent oil which cannot be any ethyl-benzene. It is possible that a small portion of the ethylene condenses with itself in the presence of the aluminum chloride before reacting with the benzene.

<sup>4</sup> Thoens, U. S. pat. 641,561, 1900.

<sup>5</sup> Ittner, U. S. pat. 1,242,445; C. A., 12, 110 (1918).

The lower viscous layer, if kept away from moisture, may be used for another run with the addition of a small amount of fresh aluminum chloride. In this way we have used the same aluminum chloride in 6 successive runs. This viscous layer appears to be analogous to the so-called "ferment" used in the manufacture of toluene from solvent naphtha.

### Results.

In Table I are given the results of 5 runs and in Table II the fractionation of the upper layer.

TABLE I

Expt.	Benzene Wt. G.	Moles	Aluminum chloride G.	Cc. per min.	Ethylene absorbed Wt. G.	Moles	Ratio
1	200	2.5	50	400-600	62	2.2	1:0.88
2	200	2.5	50	1500-2000	59	2.1	1:0.84
3	200	2.5	50	1500-2200	70	2.5	1:1
4	200	2.5	50	2500	205	7.4	1:2.96
5	700	9.0	100	2000-2500	250	8.9	1:0.99

TABLE II

#### Fractionation of the Products

Expt.	Benzene 80-100° G.	Ethyl- 100-150° G.	Di-ethyl- 150-190° G.	Tri-ethyl- 190-230° G.	Residue G.
1	52	124	54	7	5
2	56	112	56	8	14
3	42	145	67	...	15
4	0	5	72	272	38
5	236	478	167	40	21

It has been shown by Radziewanowski<sup>6</sup> and by Boedtker and Halse<sup>7</sup> that ethyl groups, as other alkyls, may be removed or shifted from one molecule to another in presence of aluminum chloride. In one experiment 250 g. of benzene and 175 g. of the fraction 230-280°, which contained the tetra-, penta-, and hexa-ethyl-benzenes were stirred and heated for 3 hours with the "ferment" remaining from a previous run in which 25 g. of aluminum chloride had been used. At first sight one would not think that stirring would aid in this reaction, but the "ferment" is very heavy and settles quickly unless the stirring is kept up. In a comparative run which was not stirred, there was little transformation.

On fractionation of the upper layer, 102 g. of benzene, 194 g. of mono-ethyl-, 77 g. of di-ethyl-benzene and 18 g. of higher compounds were obtained. It is thus possible to convert a given amount of benzene and the proper amount of ethylene almost completely into ethyl-benzene, or into the di- or tri-ethyl-benzene as desired.

### The Ethylation of Naphthalene.

By the action of ethyl chloride on naphthalene Marchetti<sup>8</sup> obtained

<sup>6</sup> Radziewanowski, *Ber.*, 27, 3235 (1894).

<sup>7</sup> Boedtker and Halse, *Bull. soc. chim.*, [4] 19, 446 (1916).

<sup>8</sup> Marchetti, *Gazz. chim. ital.*, 11, 265, 439 (1881).

ethyl-naphthalene, but in poor yield. Roux<sup>9</sup> obtained much better results if ethyl bromide and particularly if the iodide was employed, and showed that the  $\beta$  isomer is the one obtained. He tried in various ways<sup>10</sup> to substitute ethylene for the halide but could isolate no ethyl-naphthalene from the products. Fischer and Schneider<sup>11</sup> found no reaction between ethylene and naphthalene at 100–200°. We endeavored to effect this reaction by the aid of high speed stirring but without success.

Knowing that phthalic anhydride reacts with the naphthalene in a mixture of benzene and naphthalene in presence of aluminum chloride, we passed ethylene into a solution of 260 g. of naphthalene in 260 g. of benzene with 50 g. of aluminum chloride with the usual high-speed stirring at 80° but the maximum absorption was only 100 cc. per minute so this was abandoned.

Niggemann<sup>12</sup> boiled naphthalene with solvent naphtha and aluminum chloride but obtained no definite indications of the methylation of the naphthalene at the expense of the solvent. However, the ethylation of naphthalene can be readily accomplished by the transfer of ethyl groups from benzene in the presence of aluminum chloride aided by high-speed stirring, as shown by the following experiment.

A mixture of 500 g. of naphthalene, 400 g. of di-ethyl-benzene, 160 g. of ethyl-benzene, total 1060 g., and the ferment from 60 g. of aluminum chloride was stirred at 10,000 r. p. m. for 5 hours at 80°. The clear top layer was separated, washed, dried and fractionated through a good column. This gave 22 g. of benzene, 295 g. of ethyl benzene, 163 g. of diethyl benzene, 256 g. of naphthalene, 170 g. of ethyl-naphthalene, and 140 g. of higher products; total, 1046 g. That the stirring is very advantageous was shown by a parallel experiment in which a similar mixture was heated for 24 hours in a boiling water-bath without stirring. From the product 410 g. of naphthalene was recovered and only 70 g. of ethylated naphthalene products obtained.

From different runs some 700 g. of ethyl-naphthalene was prepared and, along with it, was obtained a series of fractions doubtless representing poly-ethyl-naphthalenes. The fraction 260–280° at 4 mm. deposited crystals which, after two recrystallizations from benzene and one from acetic acid, melted sharply at 179°. The supposed poly-ethyl-naphthalenes are viscous oils showing bluish-red fluorescence. The study of these must be postponed.

It is believed that other unsaturated hydrocarbons such as propylene,

<sup>9</sup> Roux, *Ann. chim. phys.*, [6] 12, 289 (1887).

<sup>10</sup> Ref. 9, p. 306, note.

<sup>11</sup> Fischer and Schneider, "Ges. Abhand. zur Kenntnis der Kohle," 1917, Vol. 1, p. 227, through *C. A.*, 13, 3183 (1919).

<sup>12</sup> Niggemann, *op. cit.*, Ref. 11, pp. 255–8, through *C. A.*, 13, 3184 (1919).

butylene, etc., will react with benzene under the same general conditions and it is intended to take up the study of these in this Laboratory.

### Summary.

1. By the aid of intensive stirring ethylene can be made to react with benzene in the presence of aluminum chloride so rapidly and completely that this becomes a practical method for the ethylation of benzene.

2. Naphthalene can be readily ethylated by heating it with poly-ethylbenzenes and aluminum chloride under intensive agitation.

BALTIMORE, MARYLAND.

[CONTRIBUTION FROM THE POLARIMETRY SECTION, BUREAU OF STANDARDS, U. S. DEPARTMENT OF COMMERCE.]

## AN IMPROVED METHOD FOR PREPARING RAFFINOSE.<sup>1</sup>

BY E. P. CLARK.

Received October 17, 1921.

Several methods have been proposed for the preparation of raffinose.<sup>2</sup> All these procedures, however, with the exception of the method of Hudson and Harding, as these authors have well pointed out, have many serious disadvantages. The latter method, while it is a decided improvement over all others, and gives fairly good results on very small lots, nevertheless has objectionable features when applied to the preparation of larger quantities of the sugar. Chief among these may be mentioned the tedious procedure in extracting the meal, the necessity of evaporating large quantities of water, due to the excessive dilution of the extract, and the quantity and cost of the reagents required. The following method overcomes these disadvantages and enables one to prepare relatively large quantities of this sugar by a convenient and economical process.

Five kg. of coarsely ground cotton-seed meal is thoroughly moistened with 2 liters of water and allowed to stand overnight. It is then loosely packed in a cylindrical percolator, and sufficient water added to saturate the meal and leave a stratum above it. When the liquid begins to run from the percolator, more menstruum is added, from time to time, until a sample of the percolate, after defecation with dry basic lead acetate, has an optical rotation of not more than 1 circular degree in a 2dcm. tube.<sup>3</sup>

<sup>1</sup> Published by the permission of the Director, U. S. Bureau of Standards.

<sup>2</sup> von Lippmann, "Die Chemie der Zuckerarten," Friedrich Viewig und Sohn, Braunschweig, 1904, 3rd ed., pp. 1627-1630. Zitkowsky, *Am. Sugar Ind.*, 12, p. 324 (1910). Hudson and Harding, *THIS JOURNAL*, 36, 2110 (1914).

<sup>3</sup> As there are substances in the meal which are extracted much more slowly than the sugar, and which cause difficulty in the subsequent steps, as well as give an inferior product, it is essential to obtain a quite rapid percolation, consuming not more than 30 to 35 minutes; and it is not expedient to carry the extraction beyond where the optical rotation of the liquid is less than 1° in a 2dcm. tube.

The process is then stopped, and the percolate is treated with a solution of basic lead acetate until no more precipitate is formed. The yellow precipitate is filtered upon large folded filters and finally washed on the filter with a little water. The filtrate and washings, which should have a volume of 12 to 13 liters, are freed from the excess of lead with oxalic acid. The lead oxalate is removed and washed on the filter with a little water. The filtrate and washings are thoroughly mixed, measured, and the optical activity of the liquid determined. It is then made distinctly alkaline to litmus with sodium hydroxide. The precipitate thus formed flocks out and settles to the bottom of the vessel in a few minutes. The supernatant liquid is next filtered through a Büchner funnel provided with a thin layer of decolorizing carbon on filter paper. The filtration is rapid under these conditions, and when all has passed through, the precipitate is placed on the filter and drained.

The raffinose is next removed from the solution by forming the insoluble calcium raffinosate. To conveniently accomplish this, the liquor is cooled to  $10^{\circ}$ , or lower, placed in a jar or other suitable container, and rapidly stirred with a mechanical stirring device. As it is being agitated, a quantity of powdered active lime, preferably 200 mesh, but not coarser than 100 mesh, sufficient to precipitate all the sugar, is slowly sifted in. After all has been added, the stirring is continued for about 5 minutes. If the lime is active, and the optical activity of the solution is calculated to raffinose hydrate with a specific rotation of about  $105^{\circ}$ , 1 g. of lime to 1 g. of raffinose is sufficient for complete precipitation. However, unless the activity of the lime is known, it is advisable to test the liquid to see whether all the sugar has been removed; if not, more lime should be added. The calcium raffinosate is filtered off, washed by grinding up to a smooth paste with 2.5 liters of cold lime water, and again filtered.

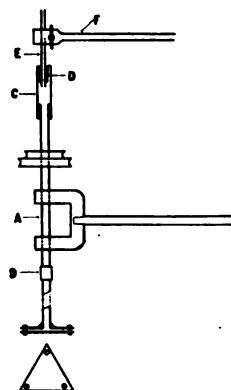


Fig. 1.

It is next carbonated to neutrality. Emphasis is to be laid upon accomplishing this easily and quickly. The device illustrated in Fig. 1 was used for this purpose.<sup>4</sup> The cake of raffinosate is placed in a deep,

<sup>4</sup> The design is essentially that developed by Mr. C. W. Doherty of the Great Western Sugar Company for carbonating beet juices. It consists of an ordinary stirring apparatus that may be clamped to any rigid laboratory support stand. The stirring shaft, A, is made of steel tubing 8 mm. inside diameter. Just below the shaft support is a union, B, to which is joined another section of shafting of the desired length. For most laboratory work, a length of 45 cm. is sufficient. Attached to the lower end are 2 triangular plates. These plates, which are 2 mm. thick and whose sides are 75 mm. long, are held 2 mm. apart by 3 rivets near the apex of the angles. The plate attached



narrow can of about 8 liters' capacity and filled  $\frac{3}{4}$  full of water at  $50^{\circ}$ , and a lively stream of carbon dioxide is passed through the apparatus while it is being turned about 1500 r. p. m. In this way the gas is centrifugally distributed and neutralizes the lime in 4 or 5 minutes without any loss of carbon dioxide. The solution is filtered while hot and the precipitate is washed by grinding up with 2 liters of water and again filtering. The combined liquors are evaporated under diminished pressure to 70–75% total solids and warmed to about  $60^{\circ}$ . To this syrup 95% ethyl alcohol is added just to saturation. The alcoholic solution is then warmed on the water-bath to about  $60^{\circ}$  and filtered through a small Büchner funnel in which has been placed a mat of washed asbestos. The filtrate, which is brilliantly clear, is seeded and placed in the ice box to crystallize. Two days are generally sufficient for complete crystallization.

The raffinose is filtered from the mother liquor, washed, first with 80%, then 95% alcohol, and dried. The yield varies considerably, according to the amount of sugar in the meal; but from a number of different experiments in which different meals were used, yields from 2.3% to 4% were obtained. The crude sugar thus prepared is quite pure, containing only from 0.06 to 0.08% ash.

To purify crude raffinose, a 40% solution (anhydrous sugar) is made by dissolving it in distilled water at  $70^{\circ}$ . The warm solution is filtered through a mat of asbestos and placed in the ice-box to crystallize. The crystals are freed from mother liquor, washed with 80%, then 95% alcohol, and dried. A sample of air-dried material thus purified contained 0.005% ash.

An alternative method of recrystallization is to concentrate the above 40% solution under reduced pressure to 70% total solids, warm to  $70^{\circ}$ , and add two volumes of 95% alcohol with constant stirring. Crystallization begins almost at once and is complete in a few hours. The crystals are filtered off, washed with 95% alcohol, and dried.

to the shafting has an opening connecting with the stirring rod. The bottom plate has no opening. C is a stuffing box made by simply attaching to the stirring shaft a short piece of good rubber tubing in which is placed a well oiled, closely fitting cork cylinder, D, through which a piece of glass tubing, E, is inserted. The glass tube is held rigid by means of a clamp, F. The cork thus arranged may be made gas-tight, and still turn freely, by tightening the rubber tubing about it with a wire.

Incidentally, this apparatus may be used to advantage for a number of purposes. In the work described in this paper, when any stirring was done, or when precipitates were ground up with water in order to wash them, the stuffing box attachment was removed and the upper orifice of the turning shaft corked. The precipitate was placed in a suitable container with the liquid used to wash it and the apparatus turned for 1 or 2 minutes. At the end of this time, the mixture was a perfectly smooth paste, all lumps being completely broken up. It has also been used very effectively in decomposing lead precipitates with hydrogen sulfide. Quantities of lead precipitates, which would normally require from 3 to 4 hours for complete decomposition, have been decomposed completely in 15 to 20 minutes,

An air-dried sample thus prepared contained 0.015% ash, and its rotation, after being completely dehydrated, was

$$[\alpha]_D^{20} = 123.23 \text{ (10.0136 g. per 100 cc.)}$$

$$[\alpha]_{\lambda=5461}^{20} = 144.95 \text{ (10.0136 g. per 100 cc.)}$$

### Summary.

An improved method for preparing raffinose from cotton-seed meal has been developed.

Cotton-seed meal is extracted by percolation. The extract is purified with basic lead acetate and the excess of lead removed with oxalic acid. The sugar is then removed from the solution as the insoluble calcium raffinosate. To regenerate the raffinose this compound is decomposed with carbon dioxide. The resulting solution is evaporated under diminished pressure to 70–75% total solids and crystallized by the addition of alcohol.

A device is described for the convenient and rapid carbonation of the raffinosate; and other uses for this apparatus are suggested.

WASHINGTON, D. C.

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[CONTRIBUTION FROM THE ROCKEFELLER INSTITUTE FOR MEDICAL RESEARCH.]

## THE SIGNIFICANCE OF THE ISO-ELECTRIC POINT FOR THE PREPARATION OF ASH-FREE GELATIN.

By JACQUES LOEB.

Received November 16, 1921.

Three years ago the writer published a paper on "the significance of the iso-electric point for the purification of amphoteric colloids"<sup>1</sup> in which it was shown that amphoteric colloids could be rendered ash-free in a simple and quick way by bringing the powdered ampholyte, *e. g.*, gelatin, to the iso-electric point and then washing a sufficient number of times with cold water. This method was based on the writer's observation that at the iso-electric point an amphoteric electrolyte like gelatin cannot combine with either anion or cation, and hence if iso-electric gelatin in powdered form be washed sufficiently all the ash formerly in combination with the gelatin can be removed. The usual procedure for preparing practically ash-free gelatin used in the writer's laboratory is as follows.

Fifty g. of commercial powdered Cooper's gelatin, which happened to possess a Sørensen value ( $P_H$ ) 6.0 to 7.0, is put into 3000 cc. of 0.0078 *M* acetic acid in a jar at 10°, and stirred frequently. After 30 minutes the supernatant liquid is decanted and fresh 0.0078 *M* acetic acid at 10° added to equal the original volume. The mass is frequently stirred and after 30 minutes the acid is again decanted and replaced by an equal volume of distilled water at 5° and a hydrogen-ion concentration a little above  $P_H$  5.0. The gelatin is well stirred and then filtered by suction through towel cloth in a Büchner funnel. It is then washed in the funnel 5 times each with 1000 cc. of water at 5°. After all the water is drained off the gelatin is transferred from the

<sup>1</sup> Loeb, *J. Gen. Physiol.*, 1, 237 (1918–19).

Büchner funnel into a large beaker which is then heated in a water-bath to about 50° till the gelatin is melted.

The concentration of the gelatin is determined by evaporating to dryness 10 cc. of the melted gelatin in an electric oven at 90° to 100° for 24 hours.

A sample of such gelatin was taken at random and the ash determined by Dr. Hitchcock of this laboratory. The stock solution of gelatin contained 12.69% of gelatin. The results of the analysis are as follows.

	Sample 1	Sample 2
Volume of solution, cc.....	20	10
Weight of dry gelatin, g.....	2.535	1.269
Weight of ash, g.....	0.0024	0.0012

Obtained qualitative tests for  $\text{Fe}^{+++}$ ,  $\text{Ca}^{++}$ , and  $\text{PO}_4^{=}$ ; negative tests for  $\text{Cl}^-$  and  $\text{SO}_4^{=}$ .

In the writer's experiments on swelling, osmotic pressure, and viscosity, 1 g. of originally iso-electric gelatin was as a rule contained in 100 cc. of solution or liquid. The ash content in this solution might have been about 1 mg. It was shown in the writer's experiments that that amount of ash (which equals roughly a 0.000033 *M* solution of tricalcium orthophosphate) has no influence on the physical properties of the proteins, such as osmotic pressure, swelling, viscosity, or potential difference.<sup>2</sup>

Miss Field<sup>3</sup> has shown that by carrying the washing process a step further, the last traces of ash can be removed from the powdered gelatin.

I had used the term "free from ionogenic impurities" instead of "ash-free" to signify the theoretical justification for the method. That my method was intended to yield ash-free gelatin was correctly understood by J. H. Northrop who used it for this purpose in his work on the digestion of gelatin<sup>4</sup> as well as by Miss Field who had seen me before the publication of her paper.

In a paper recently published in *THIS JOURNAL*, C. R. Smith<sup>5</sup> states that my results on the osmotic pressure and swelling of gelatin were vitiated by the fact that my gelatin solutions were not ash-free. This is contrary to fact as far as my papers published during the last three years are concerned. Smith refers to older papers published by me before September 1918 in the *Journal of Biological Chemistry*, and adds in the reference "also recent articles in *Am. J. Expt. Physiol.*" This is an error, since my papers on proteins during the last three years were published in the *Journal of General Physiology, Science*, and *Journal<sup>1</sup> de chimie physique*.<sup>2</sup>

The values for the osmotic pressure of solutions containing 1 g. of originally iso-electric gelatin in 100 cc. are given in a paper published in the

<sup>2</sup> Loeb, *J. Gen. Physiol.*, 1, 39, 237, 363, 483, 559 (1918-19); 2, 87 (1919-20); 3, 85, 247, 391, 547, 557, 667, 691, 827 (1920-21); 4, 73, 97 (1921-22). *Science*, 42, 494 (1920). *J. chim. phys.*, 18, 283 (1920).

<sup>3</sup> Field, *THIS JOURNAL*, 43, 667 (1921).

<sup>4</sup> *J. Gen. Physiol.*, 3, 715 (1920-21).

<sup>5</sup> Smith, *THIS JOURNAL*, 43, 1350 (1921).

May number of the *Journal of General Physiology*. Former values were lower since the solutions contained less than 1 g. in 100 cc., usually 0.8 g., as was pointed out in a paper published in January, 1921, in the same *Journal*.

I have recently shown that the osmotic pressure of a gelatin solution of a given hydrogen-ion concentration is not a constant, since it diminishes on standing on account of the formation of aggregates.

NEW YORK CITY.

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### NOTES.

**Synthesis of Indigo from Fumaric Acid and Aniline.**—In the "Text-Book of Dye Chemistry" by G. von Georgevics and Grandmougin<sup>1</sup> there is the statement that indigo has never been obtained by fusion with potash followed by air oxidation from dianilido-succinic acid  $C_6H_5.NH.CH(COOH)CH(COOH).NH.C_6H_5$ . In the course of some work on the compounds derived from maleic acid the following experiments were made which show that appreciable yields of indigo may be obtained from this compound.

**Preparation of Dibrom-succinic Acid.**—The method given by Michael<sup>2</sup> was used. Thirty g. of fumaric acid, 41.4 g. of bromine, and 26 cc. of glacial acetic acid were heated in a sealed tube at 100° for 7 hours. The contents of the tube were washed into an evaporating dish with a little acetic acid and evaporated to dryness. The average yield on three runs was 96.5%.

For the preparation of dianilido-succinic acid the method given by Reissert<sup>3</sup> was followed. The yields were 37%, 38.7% and 41.5% of the theoretical.

**Fusion of Dianilido-succinic Acid to Indigo.**—Vorländer<sup>4</sup> recorded that he secured indigo in 3 out of 40 or 50 trials by fusing the above acid with potassium hydroxide. No yields were given. The fusion of the free dianilido-succinic acid by us with a molecular mixture of potassium and sodium hydroxide (9.6 parts to 1 part of acid) in a small crucible at 450° for 1½ hours followed by air blowing failed to give a trace of indigo. Similar negative results were obtained in a closed agitated pot with the mixed caustic. However, indigo was obtained by the following procedure. A molecular mixture (300 g.) of potassium and sodium hydroxides was dehydrated at 450° for 2½ hours in a closed agitated iron pot. Thirty g. of sodamide was then added and a stream of dry ammonia passed through

<sup>1</sup> Scott, Greenwood and Co., London, 1920. Trans. from 4th German ed. by F. A. Mason.

<sup>2</sup> Michael, *J. prakt. Chim.*, [2] 52, 295 (1851).

<sup>3</sup> Reissert, *Ber.*, 26, 1763 (1893).

<sup>4</sup> Vorländer, *Ber.*, 27, 1604 (1894).

the pot. To the melt 25 g. of the sodium salt of dianilido-succinic acid was added. The temperature was held at 230–240° for 1½ hours. The melt was dissolved in water and blown with air. Indigo precipitated and was filtered off. The yield was 11.5 g. or 60.4% of that calculated on the basis of 100% indigo from pure (100%) dianilido-succinic acid, or 25% on the fumaric acid added.

This indigo was 96.5% pure by the method of Bloxam<sup>5</sup> and showed satisfactory dyeing qualities.

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Received October 6, 1921.

**The Occurrence of Terpin Hydrate in Nature.**—Terpin hydrate, ( $C_{10}H_{20}O_2 \cdot H_2O$ ), a well crystallized substance, has long been known as a product of the synthetic laboratory. It is easily prepared by allowing turpentine oil to stand in the air in contact with water for a long time or more rapidly by adding nitric acid and alcohol to the mixture. It seems strange, then, that it should not have been formed by natural agencies, yet until recently it was unknown in nature. In October, 1920, the writer described a crystalline substance, flagstaffite, found in buried pine logs, giving the result of chemical analyses, molecular weight determinations and crystallographic measurements.<sup>1</sup> At that time he was unable to find any natural or synthetic product that corresponded to it, but later, on the suggestion of Dr. Francis D. Dodge of Brooklyn, N. Y., careful comparisons were made with terpin hydrate with the result that both crystallographically and chemically they were found identical.<sup>2</sup> The discovery of this substance in logs buried at least 500 years as shown by tree rings in stumps still rooted in the debris, adds a new mineral species, while its identity with a well-known synthetic product is of general interest.

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Received November 21, 1921.

**The Action of Halogens on Aceto-acetic Ester.**—The action of chlorine and of bromine on aceto-acetic ester has been the subject of many investigations and of considerable controversy. In a series of researches extending from 1890–4 Hantzsch finally proved, by a method that is both elegant and conclusive, that the product obtained by passing chlorine into the ester is an  $\alpha$ -chloro derivative, while that obtained by adding bromine to solutions of the ester is a  $\gamma$ -bromo compound. Hantzsch also discovered that in the presence of hydrogen bromide, the  $\alpha$ -bromo ester obtained by

<sup>5</sup> Bloxam, *J. Soc. Chem. Ind.*, 25, 735 (1906).

<sup>1</sup> Guild, *American Mineralogist*, 5, 155 (1920).

<sup>2</sup> Guild, *ibid.*, 6, 133 (1921).

brominating the copper derivative passes more or less rapidly into the  $\gamma$ -bromo isomer.

I have found that when the bromination is conducted as nearly as possible in the manner in which the ester is commonly chlorinated the product is the  $\alpha$ -bromo ester. Thus when 22 g. of bromine was carried into 27 g. of aceto-acetic ester by a rapid current of air which both introduced the bromine as vapor and swept out the hydrogen bromide, the sole product was the  $\alpha$ -bromo ester: with thio-urea it gave only amino-thiazol-carboxylic ester.

The action of bromine on aceto-acetic ester is therefore exactly the same as that of chlorine, and the differences heretofore observed are due to differences in procedure.

L. I. SMITH.

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Received November 30, 1921.

**Correction.**—In the paper on "Preparation and Hydrolysis of Benzyl Esters" in the July, 1921, number of THIS JOURNAL, p. 1674, in lines 2 and 3, the words "salicylate product" should read "a product," and in line 11, the words "about 20°" should read "about -20°."

E. H. VOLWILER,  
E. B. VLIET.

CHICAGO, ILLINOIS.  
Received November 30, 1921.

## NEW BOOKS.

**Die Elektrometrische Massanalyse. (Electrometric Volumetric Analysis.)** By DR. ERICH MÜLLER, Ord. Professor and Director of the Laboratory of Electrochemistry and Physical Chemistry at the Technische Hochschule, Dresden. Theodor Steinkopff, Dresden and Leipzig, 1921. vi + 110 pp. 19 fig. 15.5 × 23 cm. Price £0-8-3.

The scope of electrometric titration has been greatly extended during the past few years by the researches of Treadwell, Dutoit, and particularly of Pinkhof and of Liebisch. Moreover, these last mentioned authors have published their results in dissertations which are comparatively inaccessible. The present volume, therefore, containing a collection and critical discussion of this material, is decidedly opportune.

In it, the author first gives a clear and simple presentation of the theoretical principles underlying this method of analysis. He includes a discussion of those requirements which must be met if a given chemical reaction is to be utilized for electrometric titration, and of those measures which can be taken if an indicator-electrode fails to respond to either of the partial reactions involved in the chemical equilibrium.

Next, the author describes 4 general methods for the execution of electrometric titrations, and considers the relative advantages and disad-

vantages of each. Many practical suggestions are made for the execution of the measurements.

Finally, the author gives a compilation of those reactions which so far have been successfully utilized for electrometric titration. The list is already an imposing one, and includes among others the determination of silver, mercury, copper, cadmium, lead, hydrogen and zinc; chlorides, bromides and iodides, singly and together; sulfides, bromates, iodates, chromates, permanganates, vanadates and ferrocyanides.

This volume should certainly be of much value to chemists who contemplate using this simple and elegant means of analysis, or who wish to study its further extension or improvement.

ARTHUR B. LAMB.

*Lehrbuch der Farbenchemie, einschliesslich der Gewinnung und Verarbeitung des Teers sowie der Methoden zur Darstellung der vor- und zwischenprodukte.* (A Treatise on Color Chemistry, including the Production and Treatment of Coal Tar as well as the Methods for the Preparation of Crudes and Intermediates.) Second revised edition. By DR. HANS TH. BUCHERER. Otto Spamer, Leipzig, 1921. xi + 636 pp. 18 X 25 cm. Price unbound, 336 M.; bound, 364 M. in England.

Bucherer's treatise on dye-chemistry, after the manner of its kind, has grown vigorously during the brief interval between the first and second editions. The revised version begins the subject at an even earlier stage than the old, because it comments on present ideas as to the nature of coal, and gives an account of the interesting experiments of Fischer and Gluud on the extraction of coal with solvents and on low temperature coking.

The first chapter, which deals with coal tar and "crudes," has been extensively re-written. It brings German statistics on production, and German methods for handling the tar up to 1920. The latter seem to have changed little during the past decade. The author repeats, apparently with little faith, the reports that by the end of the war American production of toluene had reached 70,000 tons a year. The most interesting item in the section on "new methods proposed for dealing with the by-products of coking" is the account of Feld's elegant plan for ammonia recovery.

The organic chemist, who is not primarily concerned with dyes, will naturally turn with greatest interest to the chapter on "intermediates." This is much more than a bald account of the methods used for making the substances that are most important in the dye industry. It is a scientific treatise on a large part of aromatic chemistry; but the choice of subjects as well as the order in which they are presented is different from that of a regular treatise on organic chemistry. As it is stimulating to have more or less familiar facts presented from a different point of view, most organic chemists will, like the reviewer, find much that is

suggestive in this chapter. The sections dealing with the sulfonation of naphthols and naphthyl amines, the preparation of amines by the sulfite method, and the action of sulfites on nitro compounds deserve special commendation. It seems strange that the author should devote so much space to a discussion of benzene formulas and to an exposition of the simpler facts of orientation in a text that no one who does not know at least this much organic chemistry, is able to read. Presumably, he found it easier to develop his scheme without assuming any knowledge on the part of the reader than to decide on what may safely be assumed.

The third and final chapter, which describes the synthesis of dyes, is especially well done. A long section dealing with the relation between color and constitution, and a shorter one dealing with dyeing lay the foundation for a classification of dyes and for the introduction of the special terms used in dye chemistry. Then follow a number of sections describing the methods used for getting the various classes of dyes, much the longest being devoted to vat dyes. By writing mechanisms, some of them known, others assumed as plausible for the most general methods, and treating others as variations, the author manages to secure considerable cohesion for this brittle material. An illuminating running comment explains why certain compounds are important dyes while closely related substances are valueless. The chapter ends with an interesting account of natural coloring matters which includes Wilstätter's work on the anthocyanidines even though these have no technical value.

The volume is well printed on good paper. Marginal notes indicating the subjects discussed and an excellent index increase its value for reference. In "response to many requests" the author has supplied the new edition with an extensive bibliography, which is printed at the end. If this had been incorporated in the text it would be much more valuable. Where names are not given in the text the bibliography is of little use for verifying statements of fact or examining the evidence on which conclusions are based.

The book is successful and the second edition is better than the first. The dye chemist will want it in any case; but it can also be highly recommended as a valuable addition to the library of the organic chemist who is not primarily interested in dyes.

E. P. KOHLER.





# THE JOURNAL

## OF THE

# American Chemical Society

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(Founded by Ira Remsen)

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE OHIO STATE UNIVERSITY.]

### THE COMPARATIVE VALUES OF DIFFERENT SPECIMENS OF IODINE FOR USE IN CHEMICAL MEASUREMENTS.

By C. W. FOULK AND SAMUEL MORRIS.

Received July 29, 1921.

#### Introduction.

This paper<sup>1</sup> gives the results of experiments in which iodine as ordinarily prepared as a standard in volumetric analysis was compared with iodine of atomic weight purity, the medium of comparison being a sodium thiosulfate solution.

Papers of a similar sort that were found are by Gross<sup>2</sup> and Meineke.<sup>3</sup> Gross' paper is very brief and contains none of the original data. Meineke, on the other hand, prepared a number of specimens of iodine by different methods and through the medium of a thiosulfate solution compared them with an iodine purified by the method of Stas. His technique, however,

<sup>1</sup> This is the third of a series of investigations at the Ohio State Laboratory in which some fundamental point in analytical chemistry is studied by comparing the substance or operation in question with a standard substance prepared and measured with as near an approach to "atomic weight" accuracy as may be. Other similar investigations are in progress and it is hoped in time to develop new methods of preparing standard substances and new apparatus for increasing the accuracy of the important analytical measurements. The other papers are in *THIS JOURNAL*, 36, 2360 (1914), and 40, 1664 (1918).

<sup>2</sup> Gross, *THIS JOURNAL*, 25, 987 (1903).

<sup>3</sup> Meineke, *Chem. Ztg.*, 16, 1126, 1219, and 1230 (1892).

was that of an accurate analytical procedure, rather than of a precise measurement, and therefore it seemed worth while to supplement his results by the scheme followed in this paper. Meineke's papers are rich in information about the purification of iodine and contain a wealth of experimental data.

#### Preparation of Materials.

**Water.**—"Conductivity" water was used throughout.

**Starch Indicator.**—A sterilized starch paste made by the method given in Treadwell's "Quantitative Analysis" was employed.

**Potassium Iodide.**—One of the so-called analyzed brands was used. Tests showed that no iodine was set free from its solutions under the conditions of this work.

**Hydrogen Sulfide.**—The gas was generated from ferrous sulfide with c. p. sulfuric acid. Before use it was washed 5 times with water.

**Potassium Permanganate.**—The c. p. salt was recrystallized twice in platinum. It gave no reaction for chlorine.

**The Various Specimens of Iodine.**—"ATOMIC WEIGHT" IODINE. One of the general methods of Baxter<sup>4</sup> was faithfully followed, excepting as noted below, the cycle of purification processes being carried through three times. The exceptions were (a) a modification of the apparatus for distilling iodine from a liquid mixture and (b)

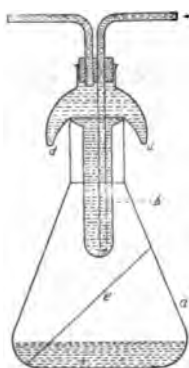


Fig. 1.

the apparatus for the final drying of the iodine at the conclusion of the wet processes of purification. The distillation apparatus is illustrated in Fig. 1. The essential feature is the condensation tube, b, about 19 mm. in diameter and long enough to project 8 or 10 cm. into the 600cc. Erlenmeyer flask, a. It is cooled by a stream of tap water, passing through it as shown in the drawing and is held in position by a bulb blown near the top. This bulb is given an umbrella shape which serves for closing the neck of the flask against loss of iodine and also for protecting it against falling dust or other contamination. By heating the mixture in the flask almost to boiling the iodine distills and solidifies on the condensation tube. There is no contamination due to bumping with consequent projection of liquid onto the iodine. A slight danger of splashing from falling drops of water that had condensed on the cold tube is eliminated by placing a narrow glass plate as shown at e. The drops strike this and glide down gently. This apparatus, which is analogous to one described in Treadwell's "Quantitative Analysis," has proved of great value in the distillation of iodine. Drying and sublimation of the iodine was effected in an apparatus made from a Hempel desiccator modified by inserting supports for carrying a number of watch glasses, and by grinding in a condensation tube which projected through the tubulure at the top. Phosphorus pentoxide was placed on the watch glasses and in the circular tray of the desiccator. Iodine to be dried is placed in a dish in the bottom of the apparatus, which is moderately warmed. The temperature of the interior at a point about midway between the top and bottom was 40°. Under these conditions iodine vapor ascends slowly over and around the phosphorus pentoxide and solidifies on the condensation tube, which is cooled with tap water. Like the distillation apparatus, this drying tower was found to have many advantages. Its use saved time because it needed no attention while in operation.

As a final note, it should be stated that all transfers of the "atomic weight" iodine

<sup>4</sup> Baxter, THIS JOURNAL, 26, 1579 (1904).

from one vessel to another that occurred in the last of the series of purification operations were made in a dust-proof box equipped with rubber sleeves.

**IODINE 2.**—Commercial iodine was ground with potassium iodide and sublimed, and the sublimation repeated without the use of potassium iodide. The final product was then ground in a mortar and placed over calcium chloride.

**IODINE 3.**—This was commercial "resublimed" iodine just as received from the laboratory store-room.

**IODINE 4.**—Iodine recovered from titration residues and from residues from the purification of iodine by the Baxter method was the starting point of this preparation. When free iodine was present in these residues it was reduced by hydrogen sulfide and the resulting hydriodic acid neutralized by sodium hydroxide. The mixture was then evaporated in the open air, treated with manganese dioxide and sulfuric acid and the iodine distilled. This iodine was then twice dissolved in potassium iodide solution and redistilled. It was dried in a vacuum desiccator over calcium chloride for one week.

**IODINE 5.**—This was the same as Iodine 4, except that it was dried in the phosphorus pentoxide apparatus.

**IODINE 6.**—This was prepared in all respects like the "atomic weight" iodine, excepting that it was not sublimed in the phosphorus pentoxide apparatus. The product from the last distillation from potassium iodide solution was, instead, placed over sulfuric acid where it remained for 93 days before it was used.

### Comparison of the Various Specimens of Iodine.

**Balance and Weights.**—A long-armed Troemner balance and a set of gold-plated brass weights with the fractional parts of platinum were used. These weights had been calibrated by the Bureau of Standards. All weighings were made at night in order to avoid the vibrations of the building. The method of tares was used throughout and it is believed that the weighings are defined to within 0.02 to 0.03 mg. Since there is no reason to suppose that the various specimens of iodine differed materially in density, weights were not reduced to a vacuum, but they were corrected for the different densities of brass and platinum, so that the values as finally given are those that would have been obtained had all of the weights been of platinum.

**Preparation of the Iodine for Weighing.**—1. In case the iodine was to be fused it was placed in a porcelain boat in the heating tube of a Richards bottling apparatus.<sup>5</sup> After passing dry air over the sample for 20 to 30 minutes, the part of the tube occupied by the boat was cautiously heated until the iodine just melted. With care the iodine could be maintained in the liquid state for one or two minutes without undue loss by volatilization. The usual procedure was to keep it fused for one minute and then push the boat into a cooler part of the tube towards the bottling chamber. The bottom of the boat being then in contact with cold glass cooled while the upper part remained warm. Iodine that had sublimed on the edges of the boat volatilized again, so that in the end the only iodine visible was the hard, glassy looking cake in the bottom of the boat. During the whole operation the current of dry air was maintained and continued until everything was completely cool. The boat was then bottled and after lying in the balance case for at least an hour was weighed. The weighing bottle and empty boat had previously been put through the same process at

<sup>5</sup> Richards and Willard, *THIS JOURNAL*, 32, 25 (1910).

least twice or until constant weight was reached. In the weighing of all samples a weighing bottle and boat as nearly as possible like those containing the iodine were used as a counterpoise.

The air passing through this bottling apparatus was first filtered through a 2-liter bottle filled with cotton wool. It next passed through an all-glass series of purifying and drying towers, the first one of which contained glass beads over which silver nitrate solution trickled, and the second was filled with sodium carbonate that had previously been fused and the fusion cake broken into pieces; next followed 4 towers of beads over which conc. sulfuric acid was kept flowing, and finally a tube filled with alternate layers of glass wool and phosphorus pentoxide.

2. When the sample of iodine was not to be fused, it was transferred from its container to the weighing bottle as quickly as possible and with cautions against contamination from dust.

**Sodium Thiosulfate Solution.**—The solution of sodium thiosulfate used throughout the work was a residuum of 5 or 6 liters from a larger lot that had been made up in December, 1918, and standardized in January, 1919, by titrating it from a volume buret against resublimed iodine prepared as described above for Iodine 2. Its value then was 0.1003 N. During the interval of 2 years the solution had stood in an uncolored glass bottle exposed to the light but protected by a soda-lime tube against acid fumes and carbon dioxide. When it assumed a rôle in this investigation it was placed in a dark room. The first hope that a thiosulfate solution as old as this had become constant was unfounded, for a few months' work showed a progression in the results that pointed to a gradual decrease in its iodine value. Accordingly, in the following table the final thiosulfate values of the various specimens of iodine are calculated to the value which the thiosulfate solution had on April 10, 1921.

The correction factor was calculated from the average thiosulfate solution values of 0.40000 g. of "atomic weight" iodine as found in Groups I and II, and from the corresponding values of Iodine 2, as found in Groups III, IV, and V in the table. This gives three comparable time intervals, which coincide well with the whole work, and from the data the average daily change in this thiosulfate solution in terms of weight of solution to react with 0.40000 g. of iodine was found to be 0.000787 g. This amount multiplied by the time in days between the date of an experiment and April 10, was added or subtracted, as the date demanded. The authors are, of course, aware that such a procedure is not to be recommended in precise measurements, but in their case it became a necessity in order to save the results. The error introduced does not destroy the value of the results as a contribution to analytical chemistry.

**Solution and Titration of the Iodine.**—Two titration flasks were employed similar in all respects excepting that one of them was closed with

a rubber stopper and the other one was entirely of glass as illustrated by Fig. 2. The ground-in stopper carried 2 tubes, a, for introducing the sodium thiosulfate solution and b, for the escape of displaced air. Loss of iodine vapor during a titration was prevented by having Tube a, dip below the surface of the liquid and by potassium iodide solution in the bends of Tube b.

The introduction of the weighed portions of iodine into this titrating flask was accomplished by first loosening but not removing the stopper of the weighing bottle and then putting the bottle into the flask. Next with the flask in an inclined position the stopper of the weighing bottle was removed with a glass hook which was quickly withdrawn and the flask closed. Two cc. of saturated potassium iodide solution was then added through Tube a, followed by a little water. By properly rotating and inclining the titrating flask the boat was brought out of the weighing bottle so that all surfaces, that is, of the weighing bottle, its stopper, which had been left in the flask, and of the boat, could be bathed in the strong potassium iodide solution. When the iodine was dissolved, the volume was made up to about 150 cc. with water and was ready for titration. This was done according to the following routine. Thiosulfate solution was added in approximately 5g. portions with intermediate mixing by shaking the flask. When all but a trace of iodine had been reduced, starch indicator was added and the titration finished.

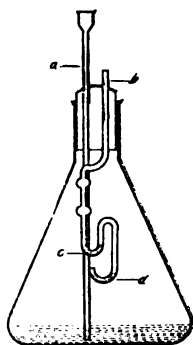


Fig. 2.

In order to reach a uniform end-point 4 comparison flasks of the same size and color of glass as the titrating flask were prepared and charged with solutions in every way like that in the titration flask at the end of a titration excepting in respect to the content of iodine. Comparison flask No. 1, contained no iodine and Nos. 2, 3 and 4 had amounts of iodine equivalent respectively, to 0.006 g., 0.012 g., and 0.018 g. of the thiosulfate solution. These varying amounts of iodine gave with starch a set of color standards by which it was easy to follow the approach of the end-point in the solution being titrated. In any event each end-point was tested by titrating back with an iodine solution.

It was found that a more uniform end-point could be obtained with the light from an ordinary tungsten bulb than with the varying light of the sun. The bulb was supported a few centimeters above the desk top with a sheet of white paper above it to reflect the light downwards upon other white paper on the desk. Upon this white surface on the desk were placed the color standard flasks and from time to time the titrating flask for comparison. The observations were made from a point above the light bulb. In this way the end-points were reproducible within 0.006 g. of the thio-

sulfate solution. Another reason for preferring artificial light to that of the sun is the action of the latter in liberating iodine. Concentrated solutions of potassium iodide became distinctly yellow in 10 minutes in direct sunlight.

TABLE I

Iodine	ANALYTICAL RESULTS					
	Iodine	Thio-sulfate solution	Thio-sulfate solution calculated to 0.40000 iodine	Average	Average corrected for change in thio-sulfate solution	Purity of iodine
G.	G.	G.	G.	G.	G.	%
Group I, April 10, 1921, "Atomic Weight" Iodine, not fused.	0.39206	32.3748	33.030			
	0.45868	37.8628	33.019			
	0.48325	39.8879	33.014	33.030	33.030	100.000
	0.49642	41.0163	33.050			
	0.57185	47.2322	33.038			
Group II, April 29, 1921, "Atomic Weight" Iodine, fused.	0.54560	35.0777	33.049			
	0.33932	28.0087	33.018			
	0.40043	33.0710	33.035	33.045	33.030	100.000
	0.57602	47.6233	33.071			
	0.49461	40.8684	33.051			
Group III, Jan. 18, 1921, Iodine 2, resublimed once from KI and once alone; ground and kept over $\text{CaCl}_2$ .	0.37134	30.6151	32.978			
	0.46267	38.1505	32.983			
	0.55278	45.6171	33.009			
	0.46183	38.0386	32.946	32.973	33.038	100.024
	0.42732	35.1963	32.946			
	0.41060	33.8484	32.975			
	0.44523	36.7008	32.972			
Group IV, Feb. 16, 1921, Iodine 2, as described above.	0.54446	44.9246	33.005			
	0.52526	43.3212	32.991	32.997	33.039	100.018
	0.46477	38.3382	32.995			
	0.46002	37.9478	32.995			
Group V, April 20, 1921, Iodine 2, as described above.	0.49583	40.9530	33.038			
	0.49537	40.9209	33.043	33.044	33.036	100.018
	0.51826	42.6567	33.051			
	0.46010	38.0061	33.042			
Group VI, Feb. 17, 1921, Iodine 3, product just as received from store-room, except that it was fused before weighing.	0.26374	21.7366	32.968			
	0.36245	29.9089	33.008	32.995	33.036	100.018
	0.34615	28.5655	33.009			
Group VII, Feb. 23, 1921, Iodine 3, as above, but not fused before weighing.	0.35231	29.0509	32.984			
	0.40486	33.4021	33.002			
	0.38186	31.4888	32.984	32.994	33.030	100.000
	0.43344	35.7709	33.011			
	0.41145	33.9214	32.977			
	0.46869	38.6702	33.003			

Group VIII, April 21, 1921,	0.45876	37.8893	33.036				
Iodine 3, as above, but not fused.	0.56198	46.4199	33.041	33.041	33.032	100.006	
	0.49452	40.8364	33.031				
	0.50921	42.0799	33.055				
Group IX, March 17, 1921,	0.45363	37.3096	32.899				
Iodine 4, recovered from residues; dried over $\text{CaCl}_2$ for one week but not sublimed.	0.28391	23.3198	32.854	32.877	32.889	99.57	
Group X, March 22, 1921,	0.36848	30.4221	33.024				
Iodine 5, same as No. 4, excepting that it was sublimed in $\text{P}_2\text{O}_5$ apparatus.	0.39392	32.5201	33.022	33.023	33.038	100.024	
	0.46061	38.0158	33.014				
	0.38952	32.1678	33.033				
Group XI, Feb. 14, 1921,	0.53442	43.9857	32.921				
Iodine 6, "Atomic Weight" Iodine; not sublimed but kept 93 days over $\text{H}_2\text{SO}_4$ .	0.40481	33.3249	32.929	32.928	32.971	99.82	
	0.42985	35.3811	32.924				
	0.42995	35.4024	32.936				
Group XII, May 5, 1921,	0.42324	34.9834	33.062				
"Atomic Weight" Iodine after 7 hours exposure in current of air saturated with water vapor.	0.50817	41.9983	33.058				
	0.54587	45.1022	33.050	33.053	33.033	100.009	
	0.49967	41.2612	33.031				
	0.43242	35.7428	33.063				

### Discussion of Results.

With the exception of Nos. 4 and 6, the specimens of iodine examined agreed within 0.02% with the "atomic weight" iodine. The deviation from the "atomic weight" iodine, except as noted, was always above 100%, which would seem to indicate such impurities as chlorine and bromine. This, however, is unlikely, since the unpurified iodine, No. 3, has a smaller positive error than the others. It would also seem from the nature of its preparation that Iodine 5 would hardly be contaminated that way. The cause is seemingly in a systematic error that has escaped detection.

Evidence of water in No. 4 is found in the fact that it rose in value when put through the phosphorus pentoxide drying tower.

The low value of No. 6 could be accounted for on the basis of a statement by Treadwell,<sup>6</sup> that iodine takes up sulfuric acid when dried over it. This statement, however, can hardly be accepted in the light of evidence to the contrary in the literature. Baxter<sup>7</sup> dried some of his atomic weight iodine over sulfuric acid and makes no mention of it as a possible impurity that was removed in the subsequent sublimation of the iodine. Meineke<sup>8</sup> reports several experiments in which iodine was exposed for days over

<sup>6</sup> Treadwell, "Quantitative Analysis," John Wiley and Sons Co., 3rd Ed., p. 646.

<sup>7</sup> Baxter, *THIS JOURNAL*, 32, 1594 (1910).

<sup>8</sup> Meineke, Ref. 3, pp. 1126, 792.



sulfuric acid without evidence that any of the acid was taken up by the iodine.

It is the belief of the authors that Iodine 6 still contained water in spite of its long exposure over sulfuric acid. An inspection of Nos. 4 and 6 shows that they had one point in common, namely, distillation from water and condensation on a cold surface on which water was condensing at the same time in contact with the iodine. This condensation in the wet way was the last purification process, except the drying (?) over a desiccating agent to which Nos. 4 and 6 were subjected. No. 4, undoubtedly contained water (see above). Lack of time and material made it impossible to test No. 6 directly, and until the point can be investigated experimentally, the hypothesis is offered that iodine when it solidifies in the presence of liquid water entrains some of the water in a way that withstands months of exposure over a desiccating agent. The complete removal of water from iodine demands dry sublimation in the presence of a desiccating agent.

**Is Iodine Hygroscopic?**—Meineke<sup>9</sup> exposed dry iodine for 5 days to the air of his laboratory and reports that the change observed could be ascribed to experimental errors. Powdered iodine exposed under a bell jar with a dish containing water took up 0.09% of water in 48 hours. Iodine crystals when subjected to the same conditions took up only 0.05% of water in 5 days. An exposure of 10 days over sulfuric acid brought these last two specimens back to 100.00%. Meineke's iodines had all been sublimed in the dry way and therefore the situation is not comparable with that of No. 6, above.

In this investigation, the following experiment was made to test the hygroscopic nature of iodine. About 5 g. of the "atomic weight" iodine was spread in a thin layer in a glass tube and a current of air previously bubbled through water was passed over it for 7 hours at the rate of about 9 liters an hour. The results are given in Group XII, of the table, and show that if any water was taken up, the amount was well within the experimental errors. This experiment and those by Meineke show that iodine is not hygroscopic to a degree that would affect analytical work.

**A Possible Contribution to the Data of Adsorption.**—One of Meineke's experiments shows that when iodine is finely divided and exposed to air saturated with water vapor, a small amount of water is taken up. It is reasonable to suppose that this water is adsorbed on the surface of the solid iodine, and the question then arises as to what effect the relatively high vapor pressure of the iodine has on such adsorption. If adsorption is a surface phenomenon, then a surface like that of an iodine crystal which is constantly sending off molecules and therefore constantly presenting a fresh surface must introduce complications. The rate of adsorption under

<sup>9</sup> Ref. 3, p. 1126.

such conditions would be slow and if later such a solid were placed in an atmosphere free from water vapor the portion adsorbed would soon be given up because the surface holding it would have disappeared. One would therefore expect solids with high vapor pressures to be slightly or not at all hygroscopic.

**The Use of a Rubber Stopper in the Titrating Flask.**—The titrations of Group VII were made in a flask closed with a rubber stopper, and those of the strictly comparable Table VIII were carried out in the all-glass apparatus. The manipulation was the same in both cases. The agreement between these two sets of results is almost perfect, and therefore the use of a rubber stopper may be permitted in analytical operations.

### Summary.

Some new forms of apparatus for the preparation and handling of pure iodine are described.

Various specimens of purified iodine were compared with a highly purified iodine. The agreement was found to be close; 0.024% was the maximum deviation.

Experiments are described which show that a rubber stopper may be used for closing the flask in which iodine is titrated.

The usual method, as given in text-books of analytical chemistry, of drying iodine by exposing it in a desiccator with a drying agent, is questioned if the iodine had previously solidified in the presence of liquid water.

The hygroscopic properties of iodine are discussed.

A suggestion is made that solids like iodine that have a measurable vapor pressure at room temperature possess peculiar adsorptive properties due to the fact that a fresh surface is being continually exposed.

COLUMBUS, OHIO.

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF VANDERBILT UNIVERSITY AND THE UNIVERSITY OF CHICAGO.]

THE PROPERTIES OF SUBSIDIARY VALENCE GROUPS. III  
THE PREPARATION, PROPERTIES AND MOLECULAR  
VOLUME RELATIONSHIPS OF THE HYDRATES  
AND AMMINES OF COBALT FLUORIDE,  
BROMIDE, IODIDE, NITRATE,  
CARBONATE AND  
CITRATE.<sup>1</sup>

BY GEORGE L. CLARK AND HENRY K. BUCKNER.

Received September 16, 1921.

In a former paper<sup>2</sup> in which the preparation, properties and molecular volume relationships of cobalt chloride and sulfate were considered, evidence was presented that the relative volumes of anion and cation in subsidiary valence compounds were of great importance in determining stability. Thus a theory, derived independently but amending and emphasizing certain of the findings of Ephraim in 25 papers,<sup>3</sup> was outlined for the existence of cavities in the space lattice<sup>4</sup> which hold the subsidiary groups and result from the packing of anion and cation in crystals. These cavities, it was pointed out, are in general larger, the greater the *difference in volume* between anion and cation, as judged by the fact that ammines are increasingly more stable in this same ratio and may actually contain more than 9 groups. It was further shown that the ammonia and water groups are compressed to the extent of 30 and 20%, respectively, of the liquid volume<sup>5</sup> when held by subsidiary valence forces in the space lattice cavities (40% for ammonia in *cobaltic*-ammines), and that in consequence there is apparent activation as shown by remarkable catalytic action of substances capable of forming ammines upon the preparation of *p*-phenylenediamine

<sup>1</sup> This paper reports chiefly some of the early work upon the general subject of Secondary valence by the senior author as National Research Fellow, but includes some experimental work upon preparation of compounds performed at Vanderbilt University, during 1920-21. The assistance of a Du Pont Fellowship held by H. K. Buckner during that time is gratefully acknowledged.

<sup>2</sup> Clark, Quick and Harkins, *THIS JOURNAL*, 42, 2483 (1920).

<sup>3</sup> Ephraim, *Ber.*, 45 to 54 (1913-21).

<sup>4</sup> The existence of cavities in certain types of space lattices has been completely confirmed by experiments, as yet unpublished, of Dr. Paul Bridgman of Harvard University.

<sup>5</sup> Assuming that the anhydrous salt which serves as a nucleus has essentially the same volume before and after  $\text{NH}_3$  and  $\text{H}_2\text{O}$  are bound. As a matter of fact the  $\text{NH}_3$  groups bound in hexammines at 25° actually occupy only  $1/1000$  the volume of the same weight of gaseous ammonia at 1 atm. pressure and the same temperature. Disregarding liquefaction, the secondary valence binding force might, therefore, be roughly equivalent to 1200 atmospheres pressure.

from *p*-dichloro-benzene and ammonia. Finally, a comparison was made between amines of cobalt salts in which the central atom has 2 valences. Although under ordinary conditions, in keeping with the Abegg-Bodländer rule, the *cobaltic* amines are more stable than the *cobaltous* by virtue of the larger stray field of the atom in its higher valence, the greater compression of the ammonia groups easily explains the fact that heat disrupts the cobaltic-amine molecule, while it has no effect on the primary valence forces in cobaltous-amines, serving merely to permit removal of the ammonia groups from the "cavities."

The present paper is concerned chiefly with the accumulation of further data bearing upon the fundamental theoretical points already presented, and enabling some new and interesting comparisons to be made. Most of the amines and ammino-hydrates to be described are entirely new. The general methods of procedure as regards precautions in preparation, analysis and determinations to the highest possible degree of accuracy of the specific gravities, were the same as in the preceding paper of this series on cobalt chloride and sulfate. Especial attention was given to the determination of the specific gravities of amines, inasmuch as numerous statements are to be found in the literature that it is impossible to carry out such exact measurements on unstable compounds when evacuation is necessary to remove adsorbed air. In an extended study, the numerical results of which will be published later, it was found that by proportioning the evacuation pressure, to which the pycnometer containing solid and liquid is subjected, to the stability of the compound, and varying the time, adsorbed gases can be removed without sensible loss of ammonia chemically combined, as shown by subsequent analysis. The temperature was of course kept as low as the freezing point of the liquid used would permit, and only small quantities of the solid in a thin layer used. Thus a reduction of pressure to 50 mm. at the freezing point of benzene easily allows the removal of adsorbed gas from cobalt or nickel halide hexamines which have a vapor pressure of ammonia reaching 760 mm. above 150°. Lower amines are handled as easily as stable hydrates. With very unstable amines such as lithium chloride tetramine, which has an atmospheric vapor pressure of ammonia at 15°, either very slight intermittent suction at low temperatures may be used, or recourse taken to the LeChatelier method of introducing a small smooth crystal into a small-bore graduated tube and measuring the change in volume of the contained liquid. In this particular case, however, accurate work is simplified by the fact that the amine is partially melted, so that a liquid already bathes the crystals and evacuation is unnecessary. Another promising method where benzene is used consists in sweeping a stream of its vapor over the solid before immersing in the liquid. A surprisingly complete removal of adsorbed gases is possible. In all cases of specific gravities reported in this

paper, the values are averages of several determinations, checked by analysis of the ammine after spontaneous evaporation of the benzene.

In studies on the hydrates and ammines of cobaltous fluoride, chloride, bromide, iodide, nitrate, carbonate and citrate it has been the attempt to follow the speed with which dry ammonia gas is absorbed by the anhydrous salt. For this work a balance was adjusted so that one of the pans swung by a fine silk thread in a chamber which was tight except for the small opening through which the thread passed. The anhydrous salt was placed upon the pan in the chamber, and perfectly dry ammonia conducted in a constant stream into the chamber. The speed of ammonia combination and the composition of the ammine could then be definitely followed by adjusting weights upon the other pan of the balance. Special precautions were taken to exclude traces of moisture, particularly in the work with cobalt fluoride. Soda lime, potassium hydroxide and metallic sodium were kept in the glass vessel enclosing the balance pan, and the stream of ammonia, dried by passing through towers of the above substances, was kept flowing rapidly enough to prevent entrance of air through the opening into the balance case, which was in turn kept closed and dry.

### Experimental.

**Cobaltous Fluoride Trihydrate.**—This compound was prepared by the action of hydrofluoric acid on an imported cobaltous carbonate. Rapid concentration of the solution in a platinum dish on the water-bath and stirring during the process of concentration caused the formation of small crystals. A crust which adhered tenaciously to the sides of the dish was discarded. The rose-red crystals obtained in this way were washed with absolute alcohol and ether and dried. Owing to the presence of sodium carbonate in the cobaltous carbonate the salt contained a small amount of sodium fluoride. Considerable difficulty was experienced in the analysis for water, as the salt is completely dehydrated only at a temperature of  $300^{\circ}$  in a stream of nitrogen. Analysis for cobalt and water gave the following results.

*Analyses.* Calc. for  $\text{CoF}_2 \cdot 3\text{H}_2\text{O}$ : Co, 39.05;  $\text{H}_2\text{O}$ , 35.79. Found: Co, 38.78 (av. 4 detns.);  $\text{H}_2\text{O}$ , 35.64 (av. 5 detns.).

The specific gravity of cobaltous fluoride trihydrate is 2.583.

No reference to a trihydrate is to be found in the literature, but the corresponding nickelous fluoride trihydrate has been prepared.<sup>6</sup> Cobaltous fluoride dihydrate and a hydrated acid salt<sup>7</sup> have been prepared and described. Poulenc<sup>8</sup> prepared cobaltous fluoride in the anhydrous condition by heating to fusion the chloride with an excess of ammonium fluoride, forming the double fluoride,  $\text{CoF}_2 \cdot 2\text{NH}_4\text{F}$ , which on further heating in an atmosphere of an inert gas yielded the anhydrous salt in an amorphous condition. Several attempts to prepare the anhydrous salt by this method were without success, the oxide being formed instead.

<sup>6</sup> Clarke, *Am. J. Sci.*, 13, 291 (1877).

<sup>7</sup> Bohm, *Z. anorg. Chem.*, 43, 326 (1905). Edmister and Cooper, *THIS JOURNAL*, 42, 2419 (1920).

<sup>8</sup> Poulenc, *Compt. rend.*, 114, 1426 (1892).

**Cobaltous Fluoride Hexammine.**—This ammine was prepared for the first time, by passing dry ammonia gas over the anhydrous salt placed on the pan of a balance as already described.

The anhydrous salt darkens within a few minutes. Forty minutes was required for the salt to take on one mole of ammonia while nearly 24 hours was required to take on the last mole, as the following table shows.

CHANGE IN COMPOSITION WITH THE TIME

Hours	Minutes	Composition	Hours	Minutes	Composition
0	0	$\text{CoF}_3$	5	45	$\text{CoF}_3 \cdot 4\text{NH}_3$
0	40	$\text{CoF}_3 \cdot \text{NH}_3$	10	9	$\text{CoF}_3 \cdot 5\text{NH}_3$
1	44	$\text{CoF}_3 \cdot 2\text{NH}_3$	23	55	$\text{CoF}_3 \cdot 6\text{NH}_3$
3	21	$\text{CoF}_3 \cdot 3\text{NH}_3$			

A total of 6.3 moles of ammonia were taken on by the anhydrous salt, the excess of ammonia probably being either absorbed or adsorbed or both. On standing in a dilute atmosphere of ammonia the ammine slowly lost ammonia.

The specific gravity determined in liquid petrolatum when the weight of the ammine showed it to contain 0.15% under the calculated value for  $\text{NH}_3$  in  $\text{CoF}_3 \cdot 6\text{NH}_3$ , is 1.744. At  $25^\circ$  cobaltous fluoride hexammine is a dark reddish-brown liquid, solidifying when cooled in an ice-salt freezing mixture. It is easily soluble in water without hydrolysis. Upon analysis absolutely no water was found present in the liquid.

It is of interest to note here another of the anomalies in the chemical nature of fluorine and its compounds. It might be expected that, due to the strong field around the molecule of cobaltous fluoride, the compound would tend to take on ammonia groups with greater rapidity than cobaltous chloride, but in fact this tendency is entirely offset by the greater compression which the ammonia groups must undergo to pack themselves into the space lattice cavities, so great being the compression that the crystal structure is completely broken down at ordinary temperatures, resulting in the liquid ammine. Anhydrous cobaltous chloride is changed to the hexammine on exposure to ammonia gas for one hour,<sup>2</sup> while nearly 24 hours is required to change the fluoride completely to a hexammine under practically the same conditions. The hexahydrate of cobaltous fluoride is not known to exist. It is not surprising then, that six ammonia groups occupying a greater volume than six water groups cannot be packed into the space lattice cavities of the crystal to form a crystalline ammine.

**Cobaltous Fluoride Tri-ammine.**—The equilibrium product resulting when the hexammine is allowed to stand in cool dry air is the tri-ammine, light pinkish-brown in color. Two samples lost practically the calculated amount for 3 molecules of ammonia. *Nickel fluoride tri-ammine*, pure steel-gray in color, exactly corresponds. When placed in a vacuum desiccator over sulfuric acid at  $40^\circ$  the tri-ammine loses ammonia continuously until the anhydrous salt remains. The hexammine and tri-ammine are therefore the only true compounds. This point is one of great interest inasmuch as all

the other halides form hexammines, di-ammines and mono-ammines (except that there is no iodide mono-ammine).

**Cobaltous Bromide Hexahydrate.**—This compound was prepared by treating cobaltous carbonate with hydrobromic acid of sp. gr. 1.49, and evaporating on a water-bath to the formation of a deep blue solution. The concentrated solution thus obtained when cooled in ice-cold water yielded purple-red crystals of the hexahydrate. The purest obtainable cobaltous carbonate was contaminated by sodium carbonate from which it could not be freed by repeated washing with water. Boiling water hydrolyzes cobaltous carbonate. The hexahydrate, therefore, contained a small amount of cubes of sodium bromide and rhombic prisms of the dihydrate. The former are less soluble and the latter more soluble than the hexahydrate. At least a dozen recrystallizations from water did not serve to free the salt from sodium bromide. The deliquescent crystals were dried between filter papers.

*Analysis.* Calc. for  $\text{CoBr}_2 \cdot 6\text{H}_2\text{O}$ : Co, 18.04. Found: 18.68.

**Anhydrous Cobaltous Bromide.**—It was found that the anhydrous salt can be easily prepared by very carefully heating the hydrated salt to  $150^\circ$ . The hexahydrate was also completely dehydrated by allowing to stand for several weeks over conc. sulfuric acid, yielding the green cobaltous bromide.

In addition the following hydrates have been described.<sup>9</sup>

$\text{CoBr}_2 \cdot 5.5\text{H}_2\text{O}$	rose-colored	$\text{CoBr}_2 \cdot 2\text{H}_2\text{O}$	purple
$\text{CoBr}_2 \cdot 5\text{H}_2\text{O}$	pink	$\text{CoBr} \cdot \text{H}_2\text{O}$	blue
$\text{CoBr}_2 \cdot 4\text{H}_2\text{O}$	reddish-violet	$\text{CoBr}_2 \cdot 0.5\text{H}_2\text{O}$	(?)

It is probable that the hexahydrate when left over the green anhydrous salt until equilibrium is reached changes to the pink pentahydrate, for a pink salt obtained in this manner after several weeks standing gave the following analysis for cobalt.

*Analysis.* Calc. for  $\text{CoBr}_2 \cdot 5\text{H}_2\text{O}$ : Co, 19.19. Found: 19.46.

Various ammino-hydrates, one corresponding approximately to the formula  $\text{CoBr}_2 \cdot 2\text{NH}_3 \cdot 7\text{H}_2\text{O}$  but more likely a mixture, were prepared by saturating strong ammonium hydroxide with cobalt bromide, adding a little alcohol and allowing the solution to evaporate spontaneously to dryness.

The hexammine has been prepared by exposing the anhydrous bromide to dry ammonia gas,<sup>10</sup> and also by leading ammonia into a solution of the salt in methyl acetate. It is possible that its preparation can be effected by any one of the three other methods described in the first paper<sup>2</sup> of this series.

The hexammine loses ammonia on heating, changing at  $120^\circ$  to a blue salt of the composition  $\text{CoBr}_2 \cdot 2\text{NH}_3$ . The  $\alpha$  and  $\beta$  forms of the di-ammine have been prepared according to the directions of Biltz and Fetkenheur,<sup>11</sup> together with the mono-ammine. An interesting new method for the preparation of the mono-ammines of cobalt chloride, not described in the former paper, and cobalt bromide was developed. This consisted in heating at  $230^\circ$  in a closed tube an intimate mixture of the corresponding hexammine and anhydrous salt in calculated proportions. During this heating a very distinct color change takes place, the chloride changing to a blue-violet and the bromide to a blue, and very definite mono-ammines of theoretical composition are obtained. In the case of cobaltous iodide, however, the final product is a mixture of the di-ammine and anhydrous salt, easily distinguishable under the microscope, and proving the non-existence of the mono-ammine of the iodide.

Cobaltous Iodide may be obtained in the anhydrous condition as a black metallic-

<sup>9</sup> Guareschi, *Atti acad. sci. Torino*, **48**, 929 (1913).

<sup>10</sup> Ephraim, *Z. physik. Chem.*, **83**, 196 (1915).

<sup>11</sup> Biltz and Fetkenheur, *Z. anorg. allgem. Chem.*, **87**, 97 (1918).

looking mass by heating cobalt in a current of iodine vapor, or by desiccation of the hydrated salt over conc. sulfuric acid *in vacuo*.<sup>13</sup> It is most readily obtained by warming the finely divided metal with water and iodine.

The hexahydrate is obtained as dark red, hexagonal prisms, by evaporating and then strongly cooling the aqueous solution. Further concentration yields the nonahydrate which crystallizes in red, rhombic plates, which lose 3 molecules of water at 6.4°.<sup>13</sup> The tetrahydrate and the dihydrate are green.

The hexammine<sup>14</sup> and two di-ammines<sup>11</sup> have been prepared.

**Cobaltous Nitrate Hexahydrate.**—A pure commercial product was used. The deliquescent crystals were placed in a desiccator over the partly dehydrated salt and left until equilibrium was established, when the product is a light reddish-brown. An analysis for cobalt shows the purity of the salt.

*Analysis.* Calc. for  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ : Co, 20.26. Found: 20.29.

The specific gravity in toluene was 1.8800; in liquid petrolatum, 1.8854; av. 1.883.

**Cobaltous Nitrate Dihydrate.**—This was obtained by allowing the hexahydrate to stand over conc. sulfuric acid for a period of 3 months. An analysis for cobalt gave the following result.

*Analysis.* Calc. for  $\text{Co}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ : Co, 26.92. Found: 26.91.

The specific gravity in liquid petrolatum was 2.397.

Attempts to prepare the trihydrate by melting the hexahydrate and keeping it at 70–74°<sup>15</sup> were unsuccessful, and instead a salt giving an analysis of 26.53% for cobalt was obtained, this value being nearly that for cobalt in the dihydrate.

Cobaltous nitrate has been obtained in the anhydrous condition by the action of nitric anhydride on the hydrated salt.<sup>16</sup>

A break in the solubility curve of the salt at –22° is attributed by Funk<sup>16</sup> to the formation of a nonahydrate.

**Cobaltous Nitrate Hexammine.**—This ammine was prepared in a very pure state by placing a small quantity of the hexahydrate in a tube which could be heated conveniently in an electric oven, and passing a rapid current of dry ammonia over it. A series of color changes takes place due to the formation of unstable intermediate compounds. The salt becomes violet at first contact with ammonia, then black, and finally assumes the original color of the hexahydrate. The last traces of water were driven out only by alternately heating to 40° and further passing of ammonia. Several hours were required for the preparation.<sup>17</sup>

The perfectly anhydrous salt is stable, but in the presence of a slight amount of moisture it gradually darkens.

The mean of two analyses for cobalt was as follows.

*Analyses.* Calc. for  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{NH}_3$ : Co, 20.68. Found: 20.68.

The specific gravity in liquid petrolatum is 1.473.

An unsuccessful attempt was made to prepare the hexammine by placing the hexahydrate on a balance pan swung in a chamber through which a current of ammonia was passed. The water of hydration was not driven out after a period of several days. A black intermediate compound was formed of the approximate composition  $\text{Co}(\text{NO}_3)_3$ .

<sup>13</sup> Hartley, *J. Chem. Soc.*, 27, 501 (1874).

<sup>14</sup> Bolschakoff, *J. Russ. Chem. Soc.*, 30, 386 (1898).

<sup>15</sup> Ephraim, *Ber.*, 46, 3742 (1915).

<sup>16</sup> Funk, *Z. anorg. Chem.*, 20, 393 (1899).

<sup>17</sup> Guntz and Martin, *Bull. soc. chem.*, 5, 1004 (1909).

<sup>18</sup> Ephraim and Rosenberg, *Ber.*, 51, 130 (1920), state that the hexammine is easily prepared in this way.



$6\text{NH}_3 \cdot 3\text{H}_2\text{O}$ . This compound was immediately hydrolyzed by water with effervescence. A rose colored compound<sup>18</sup> of this formula has been prepared in the crystalline state by the addition of ammonia in excess to a solution of cobaltous nitrate in the absence of air.

A similar black compound was prepared by putting into a pressure flask a saturated solution of cobalt nitrate, strong ammonium hydroxide and a little alcohol, and heating the flask for an hour in a bath of boiling water. On slowly cooling, the compound was deposited in the form of dark needles. Red needles were also deposited around the sides of the flask on longer standing, and were undoubtedly the crystalline hexa-ammoniate of Fremy.<sup>18</sup> They became darkened at first contact with the air. The dark needles obtained by the pressure method, when cooled to  $0^\circ$  while a current of dry ammonia was passed over it, yielded a compound of the probable formula  $\text{Co}(\text{NO}_2)_2 \cdot 6\text{NH}_3 \cdot \text{H}_2\text{O}$ .

The above compounds are very unstable. Heated on the blade of a spatula in a flame, they decompose with violence, leaving the black oxide of cobalt.

On standing for 2 months at  $20-25^\circ$  in an open vessel, the unstable hexa-ammoniate lost ammonia and water and gave a dark green compound of the formula  $\text{Co}(\text{NO}_2)_2 \cdot 3\text{NH}_3 \cdot \text{H}_2\text{O}$ . Analyses for cobalt and ammonia gave the following results.

*Analyses.* Calc. for  $\text{Co}(\text{NO}_2)_2 \cdot 3\text{NH}_3 \cdot \text{H}_2\text{O}$ : Co, 23.4;  $\text{NH}_3$ , 20.3. Found: Co, 23.1;  $\text{NH}_3$ , 20.4.

**Cobaltous Carbonate.**—An imported product was used. The sample, containing a small amount of sodium carbonate, was dried for 1.5 hours at  $105-110^\circ$ . The specific gravity in toluene was 2.818.

In an attempt to prepare pure anhydrous cobaltous carbonate, a saturated solution of the chloride was shaken in a pressure flask with a strong solution of sodium hydrogen carbonate. The stoppered flask was allowed to stand for several days, and the salt was then washed thoroughly with water. An analysis for water showed it to be a hydrate of the formula  $3\text{CoCO}_3 \cdot 2\text{H}_2\text{O}$ .

*Analysis.* Calc. for  $3\text{CoCO}_3 \cdot 2\text{H}_2\text{O}$ :  $\text{H}_2\text{O}$ , 9.17. Found: 9.19.

A crystalline salt<sup>19</sup> of the same formula has been prepared. By carrying out the reaction at low temperatures the hexahydrate is formed as small crystals. At a temperature of  $140^\circ$  the anhydrous salt is produced as a bright red powder.<sup>20</sup>

**Cobaltous Carbonate Tri-ammine Tetrahydrate.**—Anhydrous cobalt carbonate does not take on ammonia to form an ammine when placed in an atmosphere of the gas, although nickel carbonate does. By dissolving the salt in strong ammonium hydroxide and spontaneously evaporating the solution *in vacuo*, a dark red crystalline compound was prepared of probable formula  $\text{CoCO}_3 \cdot 3\text{NH}_3 \cdot 4\text{H}_2\text{O}$ . An analysis for ammonia gave the following result.

*Analyses.* Calc. for  $\text{CoCO}_3 \cdot 3\text{NH}_3 \cdot 4\text{H}_2\text{O}$ :  $\text{H}_2\text{O}$ , 29.75;  $\text{NH}_3$ , 21.1. Found:  $\text{H}_2\text{O}$ , 30.0;  $\text{NH}_3$ , 20.9.

The ammine is unstable, losing ammonia to form a lighter colored compound.

**Cobaltous Acid Citrate Dihydrate.**—A pure commercial product was used. An analysis showed it to be the dihydrate of the acid salt in which the cobalt binds 2 citrate groups.

*Analysis.* Calc. for  $\text{Co}(\text{C}_6\text{H}_7\text{O}_7)_2 \cdot 2\text{H}_2\text{O}$ : Co, 12.36. Found: 12.19.

A sample dried at  $80-85^\circ$  in a current of air for 24 hours gave as the specific gravity of the anhydrous salt 1.851 in liquid petrolatum.

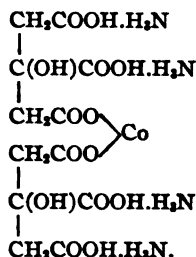
**Cobaltous Citrate Tetrammine.**—This was prepared by dissolving cobalt citrate in

<sup>18</sup> Fremy, *Ann. chim. phys.*, **35**, 257 (1852).

<sup>19</sup> H. Deville, *ibid.*, **35**, 441 (1852).

<sup>20</sup> Bertrand, *Jahrb. Miner.*, **2**, ref., 161 (1883).

strong ammonium hydroxide and evaporating spontaneously *in vacuo*. A pink and very stable crystalline ammine was produced, of the formula



It will be seen that this compound differs from the other amines described in this paper in that the ammonia groups have attached themselves to the carboxyl groups and therefore do not surround the cobalt atom.

Analyses for cobalt and ammonia are as follows.

**Analyses.** Calc. for  $\text{Co}(\text{C}_4\text{H}_7\text{O}_7)_2.4\text{NH}_3$ : Co, 11.62;  $\text{NH}_3$ , 13.38. Found: Co, 11.32;  $\text{NH}_3$ , 13.60.

The specific gravity in liquid petrolatum was 1.686.

It is quite apparent that in cobalt citrate there should be a larger difference between the volumes of the cation and anion than in the halides, and that this should enable combination with 6 or even more ammonia groups.<sup>31</sup> The citrate does form a tetrammine of great stability but no hexammine. However this is the case of an acid salt in which there are still present 4 hydrogen atoms in 4 carboxyl groups which are coordinate with and protect the cobalt atom from the exercise of its usual secondary

TABLE I

Substance	Density	Molecular vol.	Apparent volume of subsidiary group	Contraction %
KF		23.4		59.2
KCl		37.52		45.0
KBr		43.30		40.2
KI		53.16		33.3
	4.22			
$\text{CoF}_2$	4.43	23.6		27.5
$\text{CoCl}_2$	3.356	38.70		25.86
$\text{CoBr}_2$	4.91	44.79		26.3
$\text{CoI}_2$	5.68	55.04		27.3
$\text{CoF}_2.6\text{NH}_3$	1.744	114.2	$\text{NH}_3$ : 15.4	40.8
$\text{CoCl}_2.6\text{NH}_3$	1.497	154.01	19.33	26.3
$\text{CoBr}_2.6\text{NH}_3$	1.955	164.07	19.89	23.7
$\text{CoI}_2.6\text{NH}_3$	2.36	174.6	20.10	22.1
$\text{CoCl}_2.6\text{H}_2\text{O}$	1.924	123.69	$\text{H}_2\text{O}$ : 14.165	15.9
$\text{CoBr}_2.6\text{H}_2\text{O}$	2.46	132.69	14.65	18.58
$\text{CoI}_2.6\text{H}_2\text{O}$	2.90	145.06	15.01	11.2
$\text{Co}(\text{NO}_2)_2.6\text{H}_2\text{O}$	1.883	154.61		
$\text{Co}(\text{NO}_2)_2.6\text{NH}_3$	1.473	193.49		
$\text{Co}(\text{NO}_2)_2$	2.49 (calc.)	73.5 (calc.)		

<sup>31</sup> One of the authors has just prepared for the first time the compounds  $[\text{Co}(\text{NH}_3)_4][\text{Co}(\text{NO}_2)_4]$  and  $[\text{Co}(\text{NH}_3)_4][\text{Co}(\text{NO}_2)_4(\text{NH}_3)_2]$ , verifying Ephraim's experimental work showing that with anions of very large volume, octammines may be formed.

valence forces. There are several facts which point to the conclusion that in the tetrammine the ammonia groups instead of being held by the cobalt atom are actually combined with the 4 carboxyl groups in which the hydrogen atoms have not been replaced by metal: (1) the great stability of the ammine; (2) the impossibility of removing ammonia by heat without complete decomposition of the compound; (3) the absolute absence of hydrolysis when water is added, as contrasted with the very rapid hydrolysis usual for the amines; (4) the inability of dry ammonia to act upon the citrate, and the consequent preparation by the spontaneous evaporation of the solution in strong ammonium hydroxide; and (5) the much larger contraction of the ammonia groups (the volume of each is only 16) than is the case when they do not enter into the formation of ammonium ions.

### Discussion.

In considering the relationships between the cobalt compounds discussed in this and the preceding paper<sup>3</sup> the most interesting possibilities

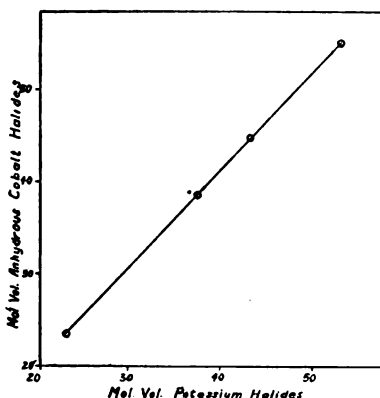


Fig. 1.

obviously are to be found in the 4 cobaltous halides and their hydrates and amines. The comparison is simplified inasmuch as with a constant metal cation are combined 4 anionic atoms which are as nearly perfectly graduated as possible from fluoride to iodide with respect to atomic volume and chemical activity or stray field of similar type. This is very beautifully shown in Fig. 1, in which the molecular volumes of the 4 potassium halides are plotted against those of the corresponding anhydrous cobalt halides. A perfectly straight line

is the result—a constant relation between the halogen atoms in compounds which could scarcely be anticipated. This method, while in a general way related to some suggestions by Fajans and Grimm,<sup>22</sup> offers splendid possibilities for the study of the halides of all metals,<sup>23</sup> allows the determination of molecular volumes and specific gravities once the slope of the line is established by known values for *two* of the halides of any particular metal, affords a check upon data on densities, is at once a criterion for the appearance of any secondary and abnormal effects peculiar to a metal and its combination with any one of the halo-

<sup>22</sup> Fajans and Grimm, *Z. Physik*, 2, 299 (1920).

<sup>23</sup> Since this paper was written in original form a paper by Biltz, *Z. anorg. allgem. Chem.*, 115, 241 (1921), has been discovered which extends the same procedure to a large number of halides besides those of cobalt and to organic derivatives, fully confirming the linearity of halogen properties. In our own work the molecular volumes of the potassium halides were used because of the undoubted accuracy of the data on densities. However by using the densities and atomic volumes of the halogens found in Table II, the molecular volumes of the cobalt halides are found to be again linear, showing that parallel relationships are maintained by the halogens free and ionic.

gens, and suggests immediately a study of other periodic group families, both metals and non-metals. In Fig. 2 the molecular volumes of the anhydrous cobalt halides are plotted as abscissas, those of the subsidiary valence compounds as ordinates. Curve *a* is for the 4 hexammines, and Curve *b* for the hexahydrates of the chloride, bromide and iodide, the corresponding fluoride hexahydrate being unknown. The curvilinear nature of both *a* and *b* is at once an experimental confirmation of the theory that although the nuclei (anhydrous halides) are in the rectilinear relationship shown in Fig. 1, and although the number of subsidiary groups

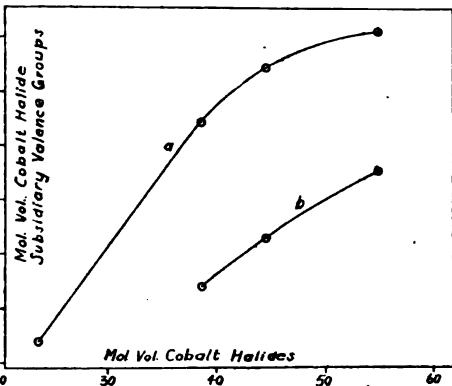


Fig. 2.

present is the same, the following effects run parallel: *the greater the difference in volume between cationic metal and anionic non-metal, the larger the cavities in the space lattice, the more stable the subsidiary valence compound and the smaller the contraction undergone by molecular groups held in the cavities.* Thus with the 4 cobalt halides the atomic volumes involved are shown in Table II.

TABLE II  
ATOMIC VOLUMES OF COBALT HALIDES  
Cobalt 6.77      At boiling point<sup>24</sup>      At T = 0°<sup>25</sup>

Fluorine.....	12.14	8.85
Chlorine.....	22.71	16.20
Bromine.....	27.04	19.20
Iodine.....	34.42	24.33

It is obvious that the scale of stability with respect to subsidiary valence unions should increase with increase in atomic weight of the halogens. Thus cobalt iodide easily forms a nonahydrate<sup>13</sup> below 6.4° while cobalt fluoride cannot even form a hexahydrate. The relative stabilities of the hexammines of the iodide, bromide and chloride have been studied by Ephraim<sup>26</sup> by determining the dissociation temperature at a definite pressure. For an ammonia pressure of 760 mm. he found respectively 471.5, 451 and 414.5° A. The hexamine of the fluoride has not been prepared or studied prior to the work of this paper. Rough measurements have indicated however that the dissociation temperature at 760 mm. is not only lower than that of cobalt chloride but falls below 300° C. The graduation in

<sup>24</sup> Landolt-Börnstein, "Tables."

<sup>25</sup> Herz, *Z. anorg. allgem. Chem.*, 105, 171 (1918).

<sup>26</sup> Ephraim, *Ber.*, 45, 1332 (1912); *Z. physik. Chem.*, 81, 513 (1913); 83, 196 (1915).

stability of the hexammines from the fluoride to the iodide is therefore clearly marked. In connection with this discussion of the effects of difference in volume between cation and anion it is interesting to note what may be the effect of substituting for cobalt, metals of both smaller and greater atomic volumes. Thus if the hypothesis is correct the nickel halide hexammines should all be *more* stable than the corresponding cobalt salts, though graduated from fluoride to iodide in the same way, since the atomic volume of nickel is smaller than that of cobalt, and the manganese compounds are *less* stable. This is clearly shown by Table III adapted from Ephraim's measurements. As a matter of fact the hexammines of nickel chloride, cobalt bromide and manganese iodide have practically the same stability, so that in case of these particular cations there is exact compensation by the halogen anions.

TABLE III

EFFECT OF DIFFERENCE IN VOLUME BETWEEN CATION AND ANION ON STABILITY OF  
SUBSIDIARY VALENCE COMPOUNDS, SHOWN BY DECOMPOSITION TEMPERATURES

	Ni	Co	Mn
(Atomic Volume).....	6.59	6.77	7.43
Iodide Hexamine.....	508.5	471.5	448.5
Bromide Hexamine.....	482	451	405
Chloride Hexamine.....	449.5	414.5	364.5

In this case the metallic atoms are quite comparable in volume and possess the same ionic charge. With other metals whose atomic volumes are greater, or the charge greater or less than 2, it is found that the maximum number of ammonia groups which can combine varies within wide limits. In Table IV these numbers are listed as experimentally determined at the present time.

TABLE IV

MAXIMUM NUMBER OF  $\text{NH}_3$  GROUPS COMBINING WITH METALLIC HALIDES.

20.  $\text{Ce}^{++}$ ,  $\text{Au}^{+++}$  (23?).
18.  $\text{Th}^{++}$ .
12.  $\text{Sm}^{+++}$ ,  $\text{Nd}^{+++}$ ,  $\text{Fe}^{+++}$ .
9.  $\text{Al}^{+++}$ .
8.  $\text{Ca}^{++}$ ,  $\text{Sr}^{++}$ .
6.  $\text{Be}^{++}$ ,  $\text{Ni}^{++}$ ,  $\text{Co}^{++}$ ,  $\text{Fe}^{++}$ ,  $\text{Cu}^{++}$ ,  $\text{Mn}^{++}$ ,  $\text{Zn}^{++}$ ,  $\text{Cd}^{++}$ ,  $\text{Mg}^{++}$ ,  $\text{Pt}^{++}$ ,  $\text{Cr}^{+++}$ ,  $\text{Co}^{+++}$ ,  $\text{Si}^{++}$ ,  $\text{Sb}^{+++}$ ,  $\text{La}^{+++}$ , metallic Ca, Sr and Ba.
4.  $\text{Li}^+$ ,  $\text{Ba}^{++}$ ,  $\text{Pb}^{++}$ ,  $\text{Te}^{++}$ ,  $\text{Sn}^{++}$ ,  $\text{Sn}^{++}$ .
3.  $\text{Tl}^{+++}$ ,  $\text{Ag}^+$ ,  $\text{Cu}^+$ ,  $\text{As}^{+++}$ ,  $\text{Bi}^{+++}$ ,  $\text{In}^{+++}$ ,  $\text{NH}_4^+$ ,  $\text{Tl}^+$ .
2.  $\text{Au}^+$ ,  $\text{Sb}^{+++}$ .
0.  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Rb}^+$ ,  $\text{Cs}^+$ ,  $\text{Ce}^{++}$ .

A cursory examination of this table shows at once that the numbers above 6 are generally associated with valence higher than 2, and hence large stray field, that 6 is associated with atomic volumes less than 14, and less than 6 groups with atomic volumes greater than 14, culminating in the entire absence of ammine formation with the large alkali metal

atoms. This is of course true only for cationic complexes, for with anionic complexes such as the polyhalides exactly the opposite rule is true and cesium tri-iodide, for example, is the most stable. Nickel iodide will not combine with iodine, but *tetrammine nickel iodide* will because the cation is large by virtue of the 4 ammonia groups.

From a further examination of Fig. 2 it is at once apparent that the ammonia groups in the hexammines are more compressible than the water groups in the hexahydrates as shown by the greater variation in the free space occupied by them. Table I gives the apparent volume occupied by each ammonia molecule in the hexammines: 20.10 in the iodide, 19.89 in the bromide, 19.33 in the chloride and only 15.4 in the fluoride—a remarkable larger contraction. This seems to be evidence that the effect of the fluorine atoms upon the secondary valence forces of the cobalt atom or upon each other is anomalous, although the primary valence union with the cobalt atom is entirely regular, at least from a molecular volume point of view. This is of course entirely possible and in keeping with the larger number of features of the chemistry of fluorine and its compounds which differentiate it from the other halogens. The interesting feature of cobaltous fluoride hexammine, however, lies in the fact that it is a *liquid* at the temperature at which all comparisons are made.<sup>27</sup> The crystal structure has been entirely broken down, and it is entirely reasonable that in the liquid an unstable ammine may exist with the ammonia groups under considerably greater compression than is usually found in space lattice cavities. It should be noted, however, that in the case of cobaltous chloride decammine discussed in the first paper of this series,<sup>2</sup> a still larger contraction of the ammonia groups is apparent. In all of the new compounds discussed in the present paper, calculations from the densities indicate that the average compressions of 30% over the free volume of ammonia as a liquid and 20% over the free volume of water are maintained, with the contraction inversely proportional to the difference in volume between acid group and cobalt. As indicated above, the volumes of the subsidiary groups are of course important in comparing the stabilities. It would be expected that an increase in volume of the molecular group would be accompanied by a decrease of residual valence affinity, greatest with the fluoride and least with the iodide. This might be shown by successive methylation of the ammonia. Ephraim<sup>28</sup> and Bonnefoi<sup>29</sup> have prepared many of these compounds and the results without exception verify the above statement. Thus  $\text{CoI}_2 \cdot (\text{NH}_2\text{CH}_3)_6$  is less stable than  $\text{CoI}_2 \cdot 6\text{NH}_3$ , but there is an increasingly greater effect in reducing stability in passing to the chloride, the

<sup>27</sup> Lithium amines, which act similarly and are particularly interesting because of atomic simplicity, will be considered in detail in the next paper of this series.

<sup>28</sup> Ephraim, *Ber.*, 46, 3742 (1913).

<sup>29</sup> Bonnefoi, *Ann. chim.*, [7] 23, 353 (1881).

cavities in the space lattice of which are necessarily smaller than in the case of the iodide.

Ephraim has made the statement that metals with atomic volumes less than 14 can form hexammines. It is clear from all work on the subject however that the strength of secondary valence forces as judged by the number of groups bound and the stability, runs as a parallel phenomenon to the following properties: (1) with constant molecular group and anion to decreasing atomic volume, ionic radius, and percentage of total volume occupied by the cation; (2) with constant molecular group, anion and cation to higher valence, and hence stray field, of the cation; (3) with constant molecular group and cation to increasing atomic or radical volume, ionic radius and percentage of total volume occupied by the anion; (4) hence to increasing difference in volume between anion and cation; and (5) with constant anion and cation to decreasing volume of the ammine molecule and to increasing values of the entropy-like ratio of critical pressure to critical temperature.

Graphically, the relationships of stability, heats of dissociation and molecular volumes of ammines and hydrates are not linear to the molecular volumes of the anhydrous salts or to the atomic volumes of the halogens if halides are being considered. There is, however, one property the importance of which in a study of secondary valence has been recognized for the first time in the work of this paper. When the *percentage contraction* undergone by an anhydrous salt and a secondary valence molecular group in forming a complex is plotted against the stability of that complex represented by the absolute temperature at which the vapor pressure reaches a given value, the graph is a straight line. This remarkable parallelism between stability and percentage contraction shows that they are determined by precisely the same influences. That the one is not determined absolutely by the other is shown by the fact that anions or cations must be closely related in order to fall on the *same* straight line. The percentage contractions of the cobalt halide complexes are given in the last column of Table I. That the linearity is not a chance one has been verified by studies so far of nickel, cadmium, copper, silver and lithium ammines, all of which give the same relationship. The same is true to an even greater extent for such anionic complexes as the polyhalides of potassium, rubidium and cesium, where, because of the fact that cations and anions are members of two families of elements uniformly related to the atoms of the rare gases of the atmosphere, all of the complexes so far studied lie on the same percentage contraction curve. Thus, the compounds  $KI.I_2$  and  $RbBr.I_2$ , which have the same stability, also have the same percentage contraction, 1.6%, which illustrates the relatively small contraction of anionic complexes. These compounds are of particular interest inasmuch as the space lattice distances for the alkaline halides are known. In the case of the two

compounds just mentioned it is clear that by starting with  $\text{RbI.I}_2$  and proceeding to  $\text{KI.I}_2$  and  $\text{RbBr.I}_2$  of equal stability the same effect is produced by changing rubidium to potassium ion, and iodide to bromide ion. As a matter of fact the difference between the ionic radii in the two cases is exactly the same. The specific data on these compounds will be reserved for a later paper. It should be observed, that the property of absolute percentage contraction is a much more rigorous one than the calculation of the apparent volume occupied by the secondary valence groups, even though interesting relative effects are possible by consideration of the latter. Thus, it has just been discovered that the ratio of the apparent volume of ammonia in lithium halide amines to the distance in Ångstrom units between the oppositely charged ions in the anhydrous salts is constant.

Finally it may be noted that sufficient knowledge of the molecular volumes of ammonia and water has now been obtained so that it is possible to calculate with a fair approximation the molecular volumes and densities of substances particularly anhydrous which are very difficult to prepare. Cobalt nitrate may be taken as an example. An examination of the position in the stability table of the hexammine of cobalt nitrate immediately leads to assigning it a volume of about 20 to each ammonia group or 120 for all six. Subtracting this from the molecular volume of the hexammine leaves 73.5 as the molecular volume of the anhydrous salt. Using this value and subtracting from the molecular volume of the hexahydrate leaves 81.2 or 13.5 for each water group, which is in very fair agreement with the average volume in hexahydrates. It is only by such a method of approximation that compounds containing both ammonia and water groups may be studied.

### Summary.

1. Further evidence has been presented bearing upon the theory previously outlined of the existence of "cavities" in the space lattice of solids, which may hold secondary valence groups, the sizes of the cavities depending upon the relative volumes of cation and anion and varying in a parallel fashion with the stability of secondary valence compounds. Particular attention has been given to the preparation, properties and relationships of all the cobalt halides. Several new compounds are reported, of chief importance among which are the hex- and tri-ammine and trihydrate of cobalt fluoride and the tetrammine of cobalt citrate.

2. Brief and preliminary consideration has been given to the methods of determining the specific gravities of unstable compounds decomposed by evacuation.

3. A new method for the ordinarily difficult preparation of mono-ammines is announced.

4. The constant relationship of physical properties among the halogens,



free and combined, is shown by the linearity of the molecular volumes of the cobalt halides, as well as those of numerous other metal halides, when plotted against the atomic volumes of the halogens at the boiling point. Such linearity is not maintained after the formation of amines or hydrates.

5. Analysis is given of 5 factors which parallel and perhaps partly determine secondary valence strength.

6. The great importance of percentage contraction in the formation of hydrates, amines and polyhalides is shown by straight line proportionality to stability.

7. The theoretical approximate calculation of molecular volumes and specific gravities of compounds very difficult to prepare is briefly outlined.

CHICAGO, ILLINOIS,  
AND NASHVILLE, TENNESSEE.

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[CONTRIBUTION FROM THE RESEARCH LABORATORY OF PHYSICAL CHEMISTRY OF THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY, No. 138.]

## THE OXIDATION OF NITRIC OXIDE AND ITS CATALYSIS.

BY CHARLES LALOR BURDICK.

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### Introduction.

In a previous article<sup>1</sup> it has been shown that the chief reactions occurring during the absorption of the oxides of nitrogen to form nitric acid in aqueous solution are the following



Reaction 1, the reaction of nitrogen peroxide with dilute aqueous nitric acid is a very rapid reaction when carried out under conditions of efficient washing action of the gas by the liquid. It is a reaction which does not, however, proceed to completion, being halted at an equilibrium condition, which in the case of nitric acid of fair concentration, is far short of complete conversion of the nitrogen peroxide. The presence of nitric oxide above a certain equilibrium concentration will prevent the reaction of absorption from proceeding at all, and only as this nitric oxide is re-oxidized and removed by the excess oxygen in the gases (according to Reaction 2) can the process of absorption go on.

Reaction 2, the re-oxidation of the nitric oxide liberated during the absorption process is a slow reaction. Since the reactions of absorption and oxidation (1 and 2) progress simultaneously, and are really mutually interdependent, it is evident that, should it be found possible by some means to cause an acceleration in the rate of the oxidation reaction, the retarding

<sup>1</sup> Burdick and Freed, *THIS JOURNAL*, 43, 518 (1921).

influence of equilibrium effects on the absorption reaction would cease to be so great a factor.

The relatively large time required by the oxidation process suggests at once that it may be feasible to cause the processes of absorption and oxidation to proceed separately. Since the absorption reaction is rapid, this can be accomplished in small units. Interposed between the small absorption units would be reaction chambers to serve as intermediate oxidizing chambers to secure complete re-oxidation of the liberated nitric oxide. With the aid of a material which catalyzes or accelerates the rate of the oxidation of nitric oxide to nitrogen peroxide it would be possible to reduce very materially the time of the oxidizing period and, therefore, the size of these reaction chambers. The following experiments were designed to determine the properties of the substances which it was anticipated might have a catalytic influence upon the reaction of oxidation.

### Description of the Experiments.

**1. Experimental Apparatus for the Study of the Possible Catalysis of Oxidation and Absorption Reactions Simultaneously.**—The experiments were an attempt to find some contact material which when wet with acid would catalyze the oxidation reaction. The material should supposedly either be of a highly absorptive character or should form unstable additive compounds with the nitrous gases, or should be readily reduced by the nitric oxide present in the gas and as readily re-oxidized by the excess oxygen.

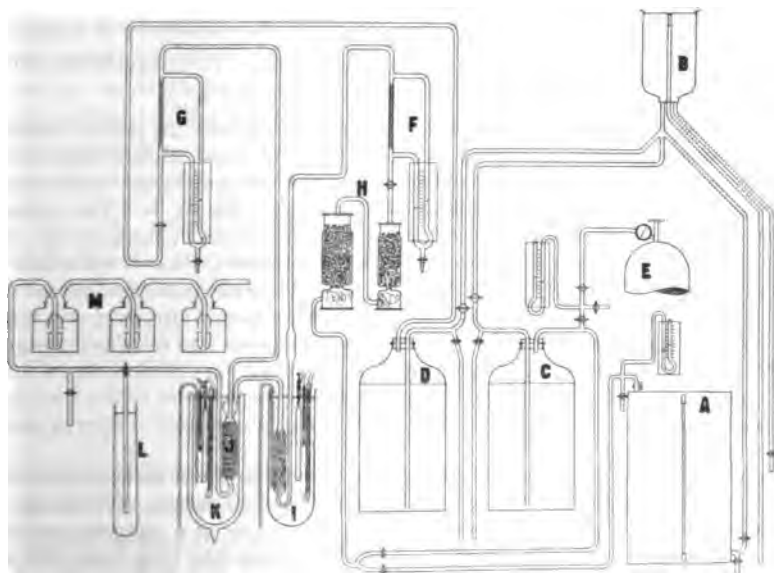


Fig. 1.

The apparatus for these experiments consisted essentially of a miniature absorption tower made completely of glass and filled with packing material crushed to 4-6 mesh. The gas current entered from the bottom and the nitric acid was circulated by means of a glass acid pump. The apparatus was essentially that of Fig. 1, with the catalyzer chamber replaced by the small absorption tower. Nitrogen peroxide from the storage reservoir and air were metered by flow gages and were mixed in a chamber. The gas was then passed in at the bottom of the tower and emerged into the alkali absorption train. A slow stream of nitric acid flowed continuously from the storage reservoir down over the contact material in the tower and out into a lower storage reservoir. From this reservoir it was again raised by the action of a glass pump to the upper reservoir. Since the quantity of acid used was always large relative to the quantity of nitrogen peroxide there was no appreciable change in the concentration of the acid.

From the analysis of the emerging gases, the percentage of the entering nitrogen peroxide which had been absorbed was computed, and the relative efficiency of the contact material determined.

The entering gas mixture contained 3% of nitrogen peroxide and 19% of oxygen, the rate of flow was 20 liters per hour and the strength of acid used was 40% by weight.

All experiments yielded negative results; that is, in no case was any improvement in absorption noted over the results obtained with a standard packing of glass fragments. The materials tested were the following: glass, pumice, charcoal, coke, and pumice impregnated with platinum, manganese dioxide, cobalt and nickel and their oxides, tungstic acid, and vanadic acid. The manganese dioxide, which is almost completely insoluble in nitric acid, dissolves readily and completely in the presence of nitrogen peroxide or nitric oxide and contaminates the acid. Practically all the other impregnating materials dissolved likewise.

**2. Experimental Apparatus for the Study of the Catalysis of Oxidation Reactions Independently of Absorption Reaction.**—The apparatus for the study of the oxidation rate of nitric oxide is shown in Fig. 1.

The oxygen-nitrogen mixture, prepared by diluting air with the proper amount of nitrogen in the measuring carboy C, was transferred by water displacement into the large storage and supply gasometer A, the gas in which was maintained under the constant head corresponding to the height of the water inlet at B. The emergent mixture of oxygen and nitrogen passed through the flowmeter F, through the water saturating apparatus in I and into the top of reaction chamber J, where it was mixed with nitric oxide from the storage carboy D, the proportion of nitric oxide admitted being regulated by the gage and valve at G. The mixed gases passed directly down through the catalyzer material in J and up through the 3-way stopcock L to the alkali absorption train M. Except when making an analysis, the gas current was deflected down into the tube L filled with alkali. The height of the liquid in L was the same as the total height in the wash bottles, so that in turning the cock no change in the rate of flow or gas proportions was produced.

To introduce water vapor into the gas the thermostat I was so arranged that it could be set to maintain any desired temperature. The gas passing through the long glass column filled with water became saturated with vapor at a temperature chosen to give the desired percentage concentration. The connecting tube from the water saturator to the reaction chamber was heated electrically to a temperature such that there was no condensation of water in the apparatus. The connection between the

reaction chamber and alkali absorption train was short and of small bore glass tubing. It was also kept warm by a heating arrangement in order that no condensation of nitric acid should take place.

Since the catalytic efficiencies of the materials tested varied over wide ranges, in order to secure a suitable degree of oxidation of the nitrous gas reaching the alkali, it was necessary to provide reaction chambers of various sizes and to vary considerably the oxygen concentration in the gas. In the experiments on inert materials (glass, coke, etc.) the reaction chamber had a volume of 30 cc., and the entering gas contained 20% of oxygen, whereas for the active charcoals the catalyzer chamber was reduced in size to 6 cc., and the oxygen concentration in the gas was kept at 3%.

The method of making a run on a new material was as follows. After the catalyzer or contact material had reached a state of equilibrium with the steady flowing current of gas (this taking nearly 24 hours in the case of the active charcoals and only a few minutes in the case of inert materials) the gas current was deflected for a period of 20 minutes to the alkali absorption train M containing a known amount of standard alkali. The analysis of the alkali,<sup>2</sup> the free volume of the contact space and the gage reading on the air gage furnished the data for calculating the reaction rate constant  $K$ . The apparatus was run continuously, analyses being made at suitable intervals. The only shut-down required was for changing the catalyzer material.

### Results of the Experimental Measurements.

The equation for the reaction of nitric oxide with oxygen,  $2\text{NO} + \text{O}_2 = 2\text{NO}_2$  indicates that the rate of oxidation will be proportional to the square of the nitric oxide concentration and directly proportional to the oxygen concentration.<sup>3</sup> The mathematical equation expressing these conditions is, therefore,

$$-dC_{\text{NO}} = K(C_{\text{O}})(C_{\text{NO}})^2 dt$$

in which  $-dC$  represents the decrease in concentration of nitric oxide in the time  $dt$ ;  $C_{\text{O}}$ , the concentration of oxygen;  $C_{\text{NO}}$  the concentration of nitric oxide at any given instant, and  $K$  the factor of proportionality, or the rate of reaction constant. The above equation transformed into form for integration is

$$-dC = K \left[ C_{\text{O}} - \frac{C_1 - C}{2} \right] C^2 dt$$

In this equation  $C_{\text{O}}$  represents the concentration of the oxygen at the time when the concentration of nitric oxide is  $C_1$ . In the case of the follow-

<sup>2</sup> For the method of analysis and calculation of gas compositions, see Ref. 1. p. 522.,

<sup>3</sup> Cf. Bodenstein and Meinecke, *Z. Elektrochem.*, 16, 876 (1910) and Brinerand Fridori, *J. chim. phys.*, 16, 280 (1918).

ing experiments  $C_0$  and  $C_1$  represent the respective concentrations of oxygen and nitric oxide at the moment of mixing.

The integrated<sup>4</sup> form of the equation is

$$Kt = \frac{2}{2C_0 - C_1} \left[ \frac{1}{C} - \frac{1}{C_1} \right] - \frac{4.6}{(2C_0 - C_1)^2} \log_{10} \frac{(2C_0 - C_1 + C)C_1}{2C_0 C}$$

Since  $K$  varies inversely as  $t$ , a large value of  $K$  indicates a high rate of oxidation and a correspondingly low value for  $t$ . The value of this number  $K$  as calculated from the experimental data is the best measure of comparative oxidation rates, and thus represents the relative efficiency of the contact material tested.

In the case of reactions catalyzed by solid substances and taking place at the surfaces of gas absorption, it does not follow that the rate of combination will be strictly according to that predicted from the chemical equation. However, in this instance since the catalytic activities of the substances investigated were tested under nearly identical conditions, the preceding equation may be accepted as sufficiently accurate for purposes of comparison.

In Table I are given the data embodying the experimental measurements of the reaction rate constant for the various substances tested. The relative reaction rates are given in the last two columns, the first giving the reaction rate constant and the second the time required for the oxidation of 90% of the nitric oxide in an arbitrarily assumed gas containing 2% nitric oxide and 3% oxygen in contact with the material under consideration. The latter figures show clearly the order of the rate of oxidation as it might actually be found in the final stages of the absorption system in an ammonia oxidation plant.

From the table it is seen that no one of the first series of substances tested exhibited any marked catalytic activity. The experiments indicate that any highly porous material has an accelerating influence on the rate. Impregnation with materials which might react chemically with the nitrous gases seemed to have no effect, for none of the samples of impregnated pumice was more effective than ordinary pumice.

The substances, metallic cobalt and nickel, their oxides and nitrates, were not found to possess any catalytic ability to oxidize the oxides of nitrogen as has been claimed by Classen.<sup>5</sup> The metals and metallic oxides are rapidly converted to nitrates, which in the presence of water vapor except at elevated temperatures, immediately deliquesce.

The influence of temperature on the rate of reaction in the presence of

<sup>4</sup> The general formula for integration is

$$Kt = \int_{c_1} \frac{dc}{c^2(k-c)} = -\frac{2}{k} \left[ \frac{1}{c} \right]_{c_1}^c - \frac{2}{k^2} \left[ \log \frac{(k-c)}{C} \right]_{c_1}^c \quad k = (a-2c_0)$$

<sup>5</sup> Classen, *Brit. pat.* 18065, 1915.

TABLE I  
EXPERIMENTAL DATA

Contact substance	Temp. ° C	Rate of flow of gas per min. Cc.	Composition of entering gas			Issuing gas NO %	Per cent. Oxida- tion in passage	Time of contact of gases with catalyzer Sec.	K	Time for 90% oxid. of 2% gas Sec.
			NO %	O <sub>2</sub> %	H <sub>2</sub> O %					
Glass container empty	0	123	3.11	20.4	0.1	0.53	83.0	19.2	21	480
	25	144	2.91	20.4	0.1	0.96	67.1	16.5	11	910
	50	159	2.74	20.4	0.1	0.91	66.9	14.9	12	840
Crushed glass	25	146	2.82	20.4	0.1	0.98	65.2	11.6	15	670
	50	148	3.45	20.3	0.1	1.19	65.4	11.0	13	770
Untreated pumice	25	137	2.97	20.4	0.1	0.86	71.0	11.9	18	560
Pumice impregnat- ed with tungstic acid in HNO <sub>3</sub>	50	142	3.06	20.4	0.1	0.78	74.6	11.5	21	480
	50	151	3.20	20.3	0.1	0.92	71.1	10.8	18	560
With tungstic acid in soln. of hydro- gen peroxide	25	143	3.04	20.4	0.1	0.92	69.9	11.5	17	590
With NiO	25	142	3.00	20.4	0.1	0.98	67.3	11.0	16	630
With CoO	25	147	2.86	20.4	0.1	1.00	65.1	11.0	15	670
With metallic Ni	25	151	3.07	20.4	0.1	0.82	73.2	11.8	19	530
With metallic Co	25	146	3.02	20.4	0.1	0.90	70.1	10.5	19	530
With MnO <sub>2</sub>	25	149	2.98	20.4	0.1	0.91	69.9	12.5	15	670
Platinized pumice	25	145	2.97	20.4	0.1	0.94	69.2	11.4	17	590
Platinized asbestos	25	158	2.62	20.4	0.1	0.75	71.4	14.2	17	590
Coke	25	147	2.62	20.4	0.1	0.78	70.1	11.3	20	500
Common charcoal	25	140	2.98	20.4	0.1	0.82	72.5	11.7	19	530
Coconut charcoal	25	140 <sup>a</sup>	3.0	20.4	0.1	0	100	11.7		
	50	140	3.0	20.4	0.1	0	100	11.7		
	80	140	3.0	20.4	0.1	0	100	11.7		
Coconut charcoal in small reaction tube	25	124.7 <sup>b</sup>	1.33	2.96	0.1	0.102	92.4	1.88	10,000	1.0
	25	118.4	1.39	2.96	0.1	0.084	94.0	1.98	12,000	0.8
	80	148.5	1.63	2.59	0.1	0.163	90.0	1.58	8800	1.1
	25	119.2	1.87	2.94	1.0	0.540	71.4	1.96	1400	7.0
	25	116.0	1.86	2.94	1.0	0.608	67.3	2.02	1100	9.0
	25	124.6	1.77	2.94	1.0	0.690	61.0	1.87	930	11.0
Coconut charcoal	50	130.7	1.31	2.96	1.0	0.48	63.3	1.64	1350	7
	80	136.6	1.96	2.90	1.0	0.39	80.0	1.71	2650	4
Peach-kernel char- coal	80	114.7	1.87	2.90	1.0	0.406	78.3	2.04	2010	5
	80	112.5	1.71	2.90	1.0	0.335	77.2	2.08	2430	4
	80	211.5	1.23	2.79	5.7	0.431	64.9	1.11	2710	4
	80	141.7	2.22	2.76	5.6	0.392	82.4	1.65	3110	3
	55	136.2	1.79	2.66	5.8	0.568	68.3	1.72	1590	6
	55	145.3	1.66	2.80	5.7	0.654	60.6	1.61	1165	9
	53	109.4	1.51	2.78	5.7	0.647	57.2	2.11	808	12
	53	120.7	1.59	2.77	5.7	0.495	68.8	3.23	910	11
	53	113.6	1.66	2.78	5.7	0.568	65.8	2.81	765	13
	100	167.9	1.27	2.45	14.7	0.305	76.0	2.00	3440	3
Steamed coke	80	105.0	2.63	2.81	3.9	1.12	57.5	3.37	329	30

<sup>a</sup> Volume of empty reaction chamber = 30 cc.<sup>b</sup> Volume of empty reaction chamber = 6 cc.inert materials is unusual.<sup>6</sup> Above 25° the rate of reaction is practically

<sup>6</sup> The temperatures recorded in the table are the temperatures maintained in the thermostat. Inasmuch as the oxidation of 1% by volume of nitric oxide in a gas is sufficient theoretically to raise its temperature 20° above the surroundings, assuming no radiation, the actual temperatures of the gases may be somewhat higher than those given.

independent of the temperature, a slight decrease in the rate of reaction with increase of temperature appearing to be the general rule. Below  $25^{\circ}$ , however, a rapid increase in the rate of reaction with decrease in temperature, was noted, the rate at  $0^{\circ}$  being twice that at  $25^{\circ}$ .

The only materials possessing catalytic properties of any pronounced value were the special charcoals and the activated coke. The two samples which were most reactive were the coconut and peach-kernel charcoals. A sample of coke subjected to steaming at  $600^{\circ}$  to  $800^{\circ}$  was found to possess a pronounced but much lower catalytic activity. It is to be expected that the highly absorptive silica gels would act in the same manner as the charcoals, but at the time these experiments were performed such material was not available for testing. The order of catalytic activity that these materials possess is quite remarkable; thus, the specific reaction rates for coconut charcoal was found to be about 11000, or more than 500 times that observed for ordinary porous materials. The time required therefore to produce a given degree of oxidation in a given gas mixture is less in the same proportion. For example, to secure the conversion to nitrogen peroxide of 90% of the nitric oxide in a gas containing 3% of nitric oxide and 3% of oxygen requires with inert material 500 seconds and in the presence of the catalyzer only 1 second.

Water vapor has a very considerable effect on the catalytic properties of the charcoals. To retain activity the catalyzer must be maintained at a temperature above the condensation point of the aqueous nitric acid which would be in equilibrium with the gas phase in contact with it. Condensation on the catalyzer or soaking in nitric acid had no permanent harmful effect, as the material after drying resumes its activity.

In Table II are tabulated experimental results to show the influence on the catalysis of the moisture content of the gases and also the effect of change in temperature. With dry gases the catalytic activity is only slightly decreased by an increase of temperature. When, however, moisture is introduced into the gases, the reaction rate drops greatly, in the case of the coconut charcoal at  $25^{\circ}$ , 1% of water vapor in the gas causing a decrease in the rate of reaction constant from 11000 to 1100. With moist gases the effect of temperature is the opposite of that found with dry gases, the rate of reaction increasing as the temperature difference above the condensation point of the aqueous nitric acid becomes greater.

A slight amount of water vapor present in the gases inhibits the activity of the catalysis to a considerable degree, but except in the immediate neighborhood of the condensation point where the catalysts are very sensitive to changes in water vapor concentrations, concentrations of water vapor in excess of 1% seem to exert no further depressing effect. Even with a water vapor content as high as 15%, as would be encountered, for instance, in the gases from ammonia oxidation, the catalytic activity

TABLE II  
EFFECT OF TEMPERATURE AND WATER VAPOR CONCENTRATION

Contact substance	Temp. ° C.	Water vapor in gas used	K Obs.
		Percentage by volume	
Coconut charcoal	25	dry	11000
	80	dry	8800
	25	1.0	1100
	50	1.0	1400
	80	1.0	2700
Peach-kernel charcoal	80	1.0	2200
	53	5.7	800
	55	5.7	2400
	80	5.7	2900
	100	14.7	3400

of the charcoals is well maintained, provided the temperature of the reaction space is sufficiently elevated.

The decrease in the rate of reaction with elevation of temperature observed in the case of the dry gases is probably occasioned by the decreased absorptive ability of the charcoal at the higher temperatures. The increase in the rate of reaction with temperature rise in the presence of water vapor is likewise probably to be explained by the lowering of the surface concentration of absorbed water on the charcoal caused by the temperature increase, thus enabling a relatively greater proportion of the active mass of the catalyzer to take up its duty.

With respect to the life of the charcoal catalysts, their properties do not seem to be impaired at all with time, tests over many weeks duration showing no decrease in activity. The charcoals were also tested for possible slow combustion, but in no case was there any evidence of carbon dioxide formation.

#### Summary.

A study of the rate of the reaction  $2\text{NO} + \text{O}_2 = 2\text{NO}_2$  has shown that ordinary porous materials either impregnated or unimpregnated possess no specific catalytic action, but that in the presence of the highly absorptive forms of carbon or charcoal the rate of the reaction may be accelerated as much as 500 fold.

The presence of water vapor in the gas mixtures greatly decreases the activity of the charcoal catalysts. Increase of the temperature interval above the point of condensation of the aqueous vapor counteracts to some extent this effect.

The temperature coefficient of the rate of reaction for the uncatalyzed and the catalyzed reaction is in general negative. For the catalyzed reaction in the presence of water vapor the temperature coefficient is apparently positive. This is probably due to the decreased absorption of water by the catalyzer at elevated temperatures.

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[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY OF THE UNIVERSITY OF PENNSYLVANIA.]

## ACTIVITY COEFFICIENTS AND COLLIGATIVE PROPERTIES OF ELECTROLYTES.

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As a result of considerable study in recent years on the thermodynamic properties of dilute and concentrated solutions of electrolytes, the author has arrived at the following means for testing the accuracy and consistency of available activity data, for calculating other thermodynamic data therefrom, and for organizing a convenient system by means of which such properties as activity coefficients, osmotic coefficients, vapor pressures and osmotic pressures may be accurately calculated. In some instances, the method suggested by Lewis and Linhart<sup>1</sup> for computing activity coefficients from freezing-point data is employed but, in the main, the present method differs from that employed by the above authors and by Lewis and Randall.<sup>2</sup> Further, the results obtained, especially for solutions of potassium and sodium chlorides, differ considerably from those of Lewis and Randall. Since these differences exist, and there will be shown to be much evidence favoring the calculations here presented, it was thought to be highly desirable to state this view of the matter.

### 1. Derivations of Equations.

In a recent communication<sup>3</sup> it was shown that the individual ion-activity coefficients (activity of the ion divided by the molal concentration) of the hydrogen, chlorine, potassium, sodium and lithium ions can be calculated by means of the empirical formula

$$\log F_a = \alpha c - \beta c^m \quad (1)$$

where  $F_a$  is the activity coefficient of the ion,  $c$  is the concentration of the electrolyte in mols per 1000 g. of water, and  $\alpha$ ,  $\beta$ , and  $m$  are constants which differ for the different ions.

The mean activity coefficient<sup>2</sup> of any electrolyte,  $F_a'$ , may also be expressed by an equation of similar form to (1). Thus

$$\log F_a' = \alpha' c - \beta' c^{m'} \quad (2)$$

where  $c$  is the molal concentration, and  $\alpha'$ ,  $\beta'$ , and  $m'$  are constants. For uni-univalent electrolytes

$$\alpha' = \frac{\alpha_1 + \alpha_2}{2}; \quad \beta' c^{m'} = \frac{1}{2}(\beta_1 c^{m_1} + \beta_2 c^{m_2})$$

where  $\alpha_1$ ,  $\beta_1$ ,  $m_1$  refer to one ion, and  $\alpha_2$ ,  $\beta_2$ ,  $m_2$  refer to the other.  $F_a'$  is defined by the equation

<sup>1</sup> Lewis and Linhart, *THIS JOURNAL*, **41**, 1951 (1919).

<sup>2</sup> Lewis and Randall, *ibid.*, **43**, 1112 (1921).

<sup>3</sup> Harned, *ibid.*, **42**, 1080 (1920).

$$F_{\pm}' = \frac{\alpha^{\pm}}{c \left( \frac{\nu^{+}}{\nu^{+} \times \nu} \right)^{\frac{1}{\nu}}}$$

In this equation  $\nu^{+}$  is the mol number of cations present,  $\nu^{-}$  is the mol number of anions present, and  $\nu$  is equal to  $\nu^{+} + \nu^{-}$  (e. g., for  $\text{BaCl}_2$ ,  $\nu^{+}=1$ ,  $\nu^{-}=2$ ; for  $\text{La}_2(\text{SO}_4)_3$ ,  $\nu^{+}=2$ ,  $\nu^{-}=3$ ) and  $\alpha^{\pm}$  is the  $\nu^{\text{th}}$  root of the product of the activities of all the ions. When the anion and cation have identical activity coefficients, Equations 1 and 2 are identical. In very dilute solutions, the term  $\alpha'c$  becomes negligible and Equation 2 approaches the form of the empirical equation of Lewis and Linhart,<sup>1</sup> namely

$$\log F_{\pm}' = -\beta' c^m. \quad (3)$$

In the present paper, Equation 2 will be used principally in testing the consistency of and in coördinating available activity data, and will be shown to be valid for all electrolytes studied throughout a concentration range from 0.0001  $M$  to 3  $M$ .

By combining Duhem's equation in its exact form and Equation 1 or 2, it becomes possible to calculate within narrow limits the vapor pressures and osmotic pressures of aqueous solutions of all electrolytes whose activity coefficients have been accurately measured. In addition, the osmotic coefficients, or, for uni-univalent electrolytes,  $i-1$ , where  $i$  is van't Hoff's  $i$ , may be computed. This purely thermodynamic quantity has usually been called "the degree of dissociation." Owing to the fact that very little reliable data are to be found on these colligative properties at 25°, it was thought highly desirable to construct a convenient and unified method for their calculation.

(a). **Vapor Pressures from the Square Root of the Activity Products of Uni-univalent Electrolytes.**—Duhem's equation may be used in the following form

$$N_1 dF_1 = -N_2 dF_2 \quad (4)$$

where  $N_1$ ,  $F_1$  are the mol fraction and free energy of the electrolyte, and  $N_2$ ,  $F_2$  are the mol fraction and free energy of the water.<sup>4</sup>  $F_1$  is related to the ion activities by

$$F_1 = RT \ln a_1 a_2 + \text{const.}$$

whence

$$dF_1 = RT d \ln a_1 a_2 \quad (5)$$

where  $a_1$  and  $a_2$  are the activities of the ions of the electrolyte. By Equation 2

$$\log F_{\pm}' = \log \sqrt{F_{\pm} F_{\pm}} = \alpha' c - \beta' c^m$$

or

$$\ln \sqrt{a_1 a_2} = 2.3026 \alpha' c - 2.3026 \beta' c^m + \ln c$$

or

$$\ln a_1 a_2 = 2 (2.3026 \alpha' c - 2.3026 \beta' c^m + \ln c) \quad (6)$$

<sup>4</sup> Lewis, *Proc. Am. Acad. Arts Sci.*, **43**, 259 (1907).

Differentiation of Equation 6 gives

$$d \ln a_1 a_2 = 2(2.3026 \alpha' dc + d \ln c - 2.3026 \beta' m' c^{m'-1} dc). \quad (7)$$

From (4) and (5) is obtained

$$N_1 d \ln a_1 a_2 = -N_2 d \ln a_2 \quad (8)$$

where  $a_2$  is the activity of the water.

Substitution of (7) in (8) gives

$$\frac{2N_1}{N_2} (2.3026 \alpha' dc + d \ln c - 2.3026 \beta' m' c^{m'-1} dc) = -d \ln a_2. \quad (9)$$

The activity of the water molecule in these solutions is related to the vapor pressure by the equation

$$\int_c^p d \ln a_2 = \int_{p_0}^p d \ln p \quad (10)$$

on the assumption that water vapor at these low pressures (about 20 mm.) obeys the ideal gas law. In the above equation,  $p_0$  is the vapor pressure of pure water and  $p$  is the vapor pressure of the solution. Consequently, the integration of the left hand member of Equation 9 will be between the limits  $c$  and 0, and the right hand member between the limits  $p$  and  $p_0$ . Further

$$N_1 = \frac{c}{55.5 + c}; \quad N_2 = \frac{55.5}{55.5 + c}$$

and

$$\frac{N_1}{N_2} = \frac{c}{55.5}$$

Hence

$$\int_c^0 \frac{2c}{55.5} (2.3026 \alpha' dc + d \ln c - 2.3026 \beta' m' c^{m'-1} dc) = - \int_{p_0}^p d \ln p. \quad (11)$$

Integration gives

$$\ln \frac{p_0}{p} = \frac{c}{55.5} \left[ 2 + 2.3026 \alpha' c - \frac{4.6052 \beta' m'}{m' + 1} c^{m'} \right]. \quad (12)$$

(b). **The General Equation for Any Electrolyte.**—In this case, we write Duhem's equation

$$N_1 d \ln a_1 a_2 \dots a_r = -N_2 d \ln a_w \quad (13)$$

where  $a_w$  is the activity of the water molecules. According to Equation 2

$$\log F_{\pm}' = \log \frac{\alpha^{\pm}}{c \left( \frac{\nu^+}{\nu^+} \frac{\nu^-}{\nu^-} \right)^{\frac{1}{\nu}}} = \alpha' c - \beta' c^{m'}$$

or

$$\ln a_{\pm} = \ln(a_1 a_2 \dots a_r)^{\frac{1}{\nu}} = 2.3026 \alpha' c - 2.3026 \beta' c^{m'} + \ln c + \frac{1}{\nu} \ln \nu^+ \nu^-$$

or

$$\ln(a_1 a_2 \dots a_r) = \nu(2.3026 \alpha' c - 2.3026 \beta' c^{m'} + \ln c + \frac{1}{\nu} \ln \nu^+ \nu^-) \quad (14)$$

Differentiation of (14) gives

$$d \ln(a_1 a_2 \dots a_r) = \nu(2.3026 \alpha' dc - 2.3026 \beta' m' c^{m'-1} dc) + d \ln c. \quad (15)$$

Substituting in (13), we obtain as before

$$\int_{55.5}^c [2.3026 \alpha' dc + d \ln c - 2.3026 \beta' m' c^{m'-1} dc] = - \int_{p_1}^p d \ln p$$

which becomes on integration

$$\ln \frac{p_0}{p} = \frac{c}{55.5} \left[ \nu + \frac{2.3026 \nu \alpha' c}{2} - \frac{2.3026 \nu \beta' m'}{m' + 1} c^{m'} \right]. \quad (16)$$

(c). **Vapor Pressures of Uni-univalent Electrolytes from Individual Ion Activities.**—Lewis<sup>4</sup> has deduced the equation

$$\frac{[N_1 d \ln a_1 + N_2 d \ln a_2 + \dots] P_1 T}{dN} = 0. \quad (17)$$

$N_1, N_2, \dots$  are the mol fractions of the molecular and ionic species of a mixture;  $a_1, a_2, \dots$ , their activities. This, as was shown by Lewis, is Duhem's equation modified so as to be thermodynamically exact. In the present case, we write

$$N_1 d \ln a_1 + N_2 d \ln a_2 + N_3 d \ln a_3 = 0 \quad (18)$$

where  $N_1, a_1$ , and  $N_2, a_2$  refer to the mol fractions and activities of the cation and anion, respectively; and  $N_3, a_3$ , the mol fractions and activities of the water molecule. From Equation 1-

$$\log \frac{a}{c} = \alpha c - \beta c^m$$

or

$$\ln a = 2.3026 \alpha c - 2.3026 \beta c^m + \ln c$$

where  $a$  is the activity of the ion. Differentiation gives

$$d \ln a = 2.3026 \alpha dc + d \ln c - 2.3026 \beta m c^{m-1} dc. \quad (19)$$

Hence

$$\left. \begin{aligned} d \ln a_1 &= 2.3026 \alpha_1 dc + d \ln c - 2.3026 \beta_1 m_1 c^{m_1-1} dc \\ d \ln a_2 &= 2.3026 \alpha_2 dc + d \ln c - 2.3026 \beta_2 m_2 c^{m_2-1} dc \end{aligned} \right\} \quad (19a)$$

where subscripts 1 and 2 refer to the cation and anion, respectively. Further

$$N_1 = N_2 = \frac{c}{55.5 + 2c}; \quad N_3 = \frac{55.5}{55.5 + 2c}.$$

Rearranging (18)

$$\frac{N_1}{N_3} [d \ln a_1 + d \ln a_2] = -d \ln a_3. \quad (18a)$$

Substitute in 18a the right hand members of Equation 19a for  $d \ln a_1$  and  $d \ln a_2$ , the values obtained above for  $N_1$  and  $N_3$ , and collect coefficients. The following is obtained,

$$\frac{c}{55.5} [2.3026(\alpha_1 + \alpha_2)dc + 2d \ln c - 2.3026\beta_1 m_1 c^{m_1-1} dc - 2.3026\beta_2 m_2 c^{m_2-1} dc] = -d \ln a_2.$$

Hence

$$\int \frac{c}{55.5} [2.3026(\alpha_1 + \alpha_2)dc + 2d \ln c - 2.3026\beta_1 m_1 c^{m_1-1} dc - 2.3026\beta_2 m_2 c^{m_2-1} dc] = - \int \frac{d \ln p}{p_0}$$

Integration of this last equation gives

$$\ln \frac{p_0}{p} = \frac{c}{55.5} \left[ 2 + \frac{2.3026(\alpha_1 + \alpha_2)c}{2} - \frac{2.3026\beta_1 m_1}{m_1 + 1} c^{m_1} - \frac{2.3026\beta_2 m_2}{m_2 + 1} c^{m_2} \right]. \quad (20)$$

(d). **Osmotic Pressures and Osmotic Coefficients.**—Let the expressions within the brackets of the right hand members of Equations 12, 16, and 20 equal  $[i]$ . Then

$$\ln \frac{p_0}{p} = \frac{c}{55.5} [i]. \quad (21)$$

The osmotic pressure can be calculated from the vapor pressure (neglecting the small term due to the compressibility of the solvent) by the formula

$$\pi = \frac{RT}{V_0} \ln \frac{p_0}{p} = \frac{RT}{V_0} \frac{c}{55.5} [i] \quad (22)$$

where  $\pi$  is the osmotic pressure,  $V_0$  the molal volume of the water at temperature  $T$  and  $R$  is the gas constant. On inspection, it is seen that  $[i]$  is van't Hoff's  $[i]$ , and that  $\left(\frac{i-1}{v-1}\right)$  is equal to the osmotic coefficient  $f_0$ ,<sup>5</sup> or the classic degree of dissociation. At 25° Equation 22 reduces to

$$\pi \text{ (atms.)} = 24.42 c [i], \quad (23)$$

on substituting 298.1 for  $T$ , 0.08207 for  $R$ , and 0.018053 for  $V_0$ .

## 2. The Activity Coefficients of Potassium Chloride Solutions.

In order to determine the parameters of Equation 2 and thus the activity coefficients of potassium chloride solutions, a method has been adopted which combines the method suggested by Lewis and Linhart<sup>1</sup> for computing activity coefficients from freezing-point data with the method employed by the author<sup>3</sup> for computing the same at higher concentrations from electromotive-force measurements. Lewis and Linhart found that, in dilute solutions of all electrolytes, the following empirical relationship holds, namely,

$$\log \left( \nu \lambda - \frac{\theta}{c} \right) = \alpha_1' \log c + \log \beta_1' \quad (24)$$

where  $\nu$  is as before the number of different ions produced in the solution by the dissociating substance,  $\lambda$  the molal freezing-point lowering of water (1.858° C.),  $\theta$  the freezing-point lowering,  $c$  the concentration, and  $\alpha_1'$  and  $\beta_1'$  are constants ( $\alpha_1'$ ,  $\beta_1'$  are the constants  $\alpha_1$ ,  $\beta_1$  in Lewis and Linhart's

<sup>5</sup> Bjerrum, *Z. anorg. Chem.*, 109, 275 (1920).

paper). By plotting  $\log\left(\nu\lambda - \frac{\theta}{c}\right)$  against  $\log c$ , straight lines are obtained from which the values of  $\alpha_1'$  and  $\beta_1'$  can be evaluated. By combining this equation with the thermodynamic equation

$$\int d \ln F'_a = \frac{1}{\nu\lambda} \int \frac{d\theta}{c} \quad (25)$$

which relates the activity coefficient with the freezing-point lowering in dilute solutions, and integrating between the proper limits, they obtained

$$\log F'_a = - \frac{\beta_1'(\alpha_1' + 1)c^{\alpha_1'}}{2.3026 \nu\lambda \alpha_1'} \quad (26)$$

Since for a given electrolyte  $\alpha_1'$ ,  $\beta_1'$ ,  $\nu$ , and  $\lambda$  are constants, this equation is equivalent to (3) where

$$\beta' = \frac{\beta_1'(\alpha_1' + 1)}{2.3026 \nu\lambda \alpha_1'}; \text{ and } m' = \alpha_1'. \quad (27)$$

Thus, by plotting freezing-point data in accordance with Equation 24, the parameters  $\beta'$  and  $m'$  of Equation 2 may be evaluated. Employing this method with solutions of potassium chloride, Lewis and Linhart obtained  $\alpha_1' = 0.535$ ;  $\beta_1' = 1.223$  which according to Equations 27 give the values  $\beta' = 0.401$ ;  $m' = 0.535$ . The author obtained  $\beta' = 0.318$  and  $m' = 0.397$ , calculated from electromotive-force data and based on the value  $F'_{a(0.1)} = 0.754$  at 0.1 *M* concentration of Noyes and MacInnes;<sup>6</sup> Lewis and

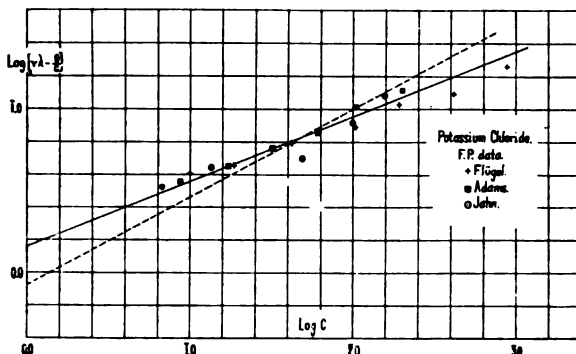


Fig. 1.

Randall<sup>2</sup> obtained  $F'_{a(0.1)} = 0.798$ . The large differences between the values of these constants as determined by Lewis and Linhart and by the author make a recalculation imperative. Instead of basing the calculation entirely upon the freezing-point data of Adams,<sup>7</sup> it was thought preferable to include also the data of Flügel<sup>8</sup> and of Jahn.<sup>9</sup> In Fig. 1, the values of

<sup>6</sup> Noyes and MacInnes, *THIS JOURNAL*, **42**, 239 (1920).

<sup>7</sup> Adams, *ibid.*, **37**, 494 (1915).

<sup>8</sup> Flügel, *Z. physik. Chem.*, **79**, 585 (1912).

<sup>9</sup> Jahn, *ibid.*, **59**, 35 (1907).

$\log \left( \nu \lambda - \frac{\theta}{c} \right)$  are plotted against  $\log c$ . It can be seen that these points group along a straight line between  $\log c = 1.00$  and  $\log c = 2.00$ , and lie near a straight line at lower concentrations. At concentrations above  $0.1 M$ , Equation 24 is no longer valid. The dotted line represents the straight corresponding to values of  $\alpha_1'$  and  $\beta_1'$  obtained by Lewis and Linhart. Their plot passes through some points obtained from Adams' data, and does not represent the line drawn through the points of all the data. The representative curve gives  $\alpha_1' = m' = 0.394$  and  $\beta_1' = 0.692$  from which, by (27),  $\beta' = 0.286$ . Employing these values in Equation 3  $F'_{a(a)} = 0.766$ . But Equation 3, is not applicable up to concentrations as high as  $0.1 M$ , and consequently, in order to obtain a more exact value for  $F'_{a(a)}$ , Equation 2 is employed, assigning to  $\alpha'$  the value  $0.070$ , and to  $\beta'$  and  $m'$  the values obtained above. In the previous article,  $\alpha'$  was assigned the value  $0.080$ . The corrected value for  $F'_{a(a)}$  is  $0.779$ . Using this value, the activity coefficients have been computed at higher concentrations from the electromotive force data of Noyes and MacInnes<sup>6</sup> and Harned<sup>10</sup> and compiled in Table I.

TABLE I  
ACTIVITY COEFFICIENTS FROM ELECTROMOTIVE FORCE DATA

$c$	$F_a'$ (obs.)		$F_a'$ (calc.)
Noyes and MacInnes		Harned	$\alpha' = 0.070$
			$\beta' = 0.292$
			$m' = 0.396$
0.03	0.851	...	0.858
0.05	0.816	...	0.821
0.10	0.779	0.779	0.776
0.20	0.723	...	0.724
0.30	0.695	0.687	0.693
0.50	0.659	0.660	0.652
0.70	0.639	...	0.625
0.75	...	0.619	0.620
1.00	0.613	0.598	0.600
1.50	...	0.575	0.578
2.00	...	0.566	0.570
2.50	...	0.568	0.567
3.00	...	0.575	0.574

The observed values are lower in all cases than those given in Table XIV in Lewis and Randall's paper. The parameters  $\alpha'$ ,  $\beta'$ ,  $m'$  can be derived from these data by the method previously employed by the author. Thus

$$\log F_a' = \alpha'c - \beta'c^m \quad (2)$$

By transposition is obtained

$$\left[ -\frac{\log F_a'}{c} + \alpha' \right] = B'c^{m-1}$$

<sup>10</sup> Harned, THIS JOURNAL, 38, 1986 (1916).

and taking the logarithms

$$\log \left[ -\frac{\log F_{\alpha'}}{c} + \alpha' \right] = \log \beta' + (m' - 1) \log c. \quad (2a)$$

Thus, the plot of  $\log \left[ -\frac{\log F_{\alpha'}}{c} + \alpha' \right]$  against  $\log c$  should be a straight

line. The plot was made by assigning different values to  $\alpha'$  until a straight line was obtained.  $m'$  can readily be determined from the slope, and  $\beta'$  from the value of  $\log \beta'$  at  $\log c = 0$  or  $c = 1$ . Fig. 2 gives this plot from which are obtained  $\alpha' = 0.070$ ;  $\beta' = 0.292$ ; and  $m' = 0.396$ . From freezing-point measurements,  $\beta' = 0.286$ , and  $m' = 0.394$ . The agreement is excellent. Using the data of Lewis and Randall<sup>2</sup> (Table XIV), and plotting

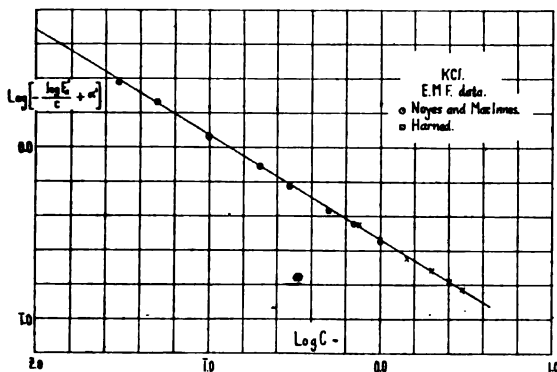


Fig. 2.

in the same way as above, a straight line is obtained which gives  $\alpha' = 0.134$ ,  $\beta' = 0.334$ , and  $m' = 0.474$ . In what follows, it will be shown that the lower values obtained by the author are more exact. The only lack of concordance between the above calculation and observed data occurs in the electromotive-force measurements of Noyes and MacInnes below  $0.01 M$ . Lewis and Randall suggest that electromotive-force measurements at these low concentrations are not reliable owing to side reactions. At present, there are not sufficient data from different sources to decide this question definitely. Having determined the values of  $\alpha'$ ,  $\beta'$  and  $m'$ , we are now in a position to compare the results with other carefully determined data.

By computing the values of the expression inside the bracket of the right hand member of Equation 12 and subtracting 1 from these values, the osmotic coefficients at the different concentrations are obtained. Equation 12 becomes on substituting the values for  $\alpha'$ ,  $\beta'$  and  $m'$  obtained above

$$\ln \frac{p_0}{p} = \frac{c}{55.5} [2 + 0.1612c - 0.3815c^{0.396}] \quad (12a)$$

whence

$$f_0 = 1 + 0.1612c - 0.3815c^{0.396}. \quad (12b)$$



Table II, Col. 2 contains the values of  $f_0$  at the concentrations denoted in Col. 1 calculated by (12b). Col. 3 contains the values of  $f_0$  using the values of  $\alpha'$ ,  $\beta'$  and  $m'$  from Lewis and Randall's data. The last two columns of this table contain values of  $f_0$  at  $0^\circ$  and  $20^\circ$  calculated by means of Equation 21 from values of  $\ln \frac{p_0}{p}$ . The latter data were obtained from Table II in a recent paper by Lovelace, Frazer, and Sease.<sup>11</sup> The values at  $0^\circ$  were calculated by them from freezing-point lowerings using an exact thermodynamic formula given by Washburn,<sup>12</sup> the freezing-point data of Roloff<sup>13</sup> and the compilation of Noyes and Falk.<sup>14</sup> The  $20^\circ$  values were obtained from their own vapor-pressure measurements.

TABLE II  
OSMOTIC COEFFICIENTS

(1) Conc.	(2) E.m.f. and f. p. 25° $\alpha' = 0.070$ $\beta' = 0.292$ $m' = 0.396$	(3) Lewis and Randall 25° $\alpha' = 0.134$ $\beta' = 0.334$ $m' = 0.474$	(4) F. p. data 0°	(5) V. p. 20° (Obs.) Eq. 28 (Mannite) (Obs.) L. F. and S.	
0.001	0.976	...	...	...	.....
0.010	0.940	0.951	...	...	.....
0.050	0.892	0.903	0.891	0.885	(0.840)
0.100	0.863	0.877	0.857	0.846	(0.815)
0.300	0.812	0.821	0.810	0.799	(0.782)
0.500	0.791	0.820	0.794	0.790	(0.774)
0.750	0.781	0.826	0.762	...	0.786
1.000	0.780	0.844	0.748	...	0.788
1.500	0.792	0.900	0.764	...	0.794
2.000	0.820	0.973	0.763	...	0.823
2.500	0.855	1.055	0.765	...	0.844
3.000	0.894	1.145	0.805	...	0.868
4.000	0.984	...	...	...	.....

Lewis and Randall's values are higher than any of the other series of results. The above data reveal that the plot of the osmotic coefficients against the concentrations will have a minimum. The plot of the molecular vapor-pressure lowerings against the concentrations will also have a minimum at the same concentration.

The empirical equation which relates the osmotic coefficient to the concentration is

$$f_0 = 1 + \alpha'c - \beta'c^m \quad (12c)$$

<sup>11</sup> Lovelace, Frazer and Sease, *THIS JOURNAL*, 43, 102 (1921).

<sup>12</sup> Washburn, "Principles of Physical Chemistry," McGraw Hill Book Co., 1915, p. 169.

<sup>13</sup> Roloff, *Z. physik. Chem.*, 18, 578 (1895).

<sup>14</sup> Noyes and Falk, *THIS JOURNAL*, 32, 1020 (1910).

where  $\alpha''$  and  $\beta''$  are the numerical coefficients in Equation 12b and  $m'$  is the same as in the previous equations. Differentiating (12c) with respect to  $c$  and equating the right hand member of the resulting equation to 0, the following is obtained as a condition for a minimum

$$\alpha'' = \beta'' m' c^{m'-1}. \quad (12d)$$

Employing this latter equation, it was found that the minimum of the results in Table II, Col. 2 occurs at  $c$  equals 0.898. The minimum from Lewis and Randall's data occurs at  $c$  equals 0.525. Lovelace, Frazer and Sease obtained a minimum in the molecular vapor-pressure-lowering—concentration plot ( $20^\circ$ ) in the neighborhood of 1  $M$  concentration.

The last column in Table II contains a series of osmotic coefficients of potassium chloride solutions at  $20^\circ$ , computed from measurements of vapor-pressure lowerings obtained by Lovelace, Frazer and Sease.<sup>11</sup> The agreement between these results and the values obtained by the author and given in Col. 2 is good but not entirely satisfactory. At concentrations from 0.05  $M$  to 0.5  $M$  their results are lower than those obtained by the author, from 0.5  $M$  to 2  $M$  their values are slightly higher; and from 2  $M$  up their results are lower. The  $5^\circ$  difference in temperature will cause some difference which would depend on the sign of the reversible molal heat of dilution by water. Since the latter quantity is negative for potassium chloride solutions, the osmotic coefficients should be higher at  $25^\circ$  than at  $20^\circ$ . In the results at concentrations from 0.5 to 2  $M$  the slight error may be in either the vapor-pressure or electromotive force measurements. The results from the data of Lovelace *et al.* at 0.05  $M$  and 0.1  $M$  are unquestionably low. This is verified by comparison with the values obtained by the above authors from measurements of both potassium chloride and mannite solutions, where any small error due to their apparatus would be partially eliminated. Since mannite solutions obey Raoult's law within narrow limits,  $f_0$  may be calculated by the equation

$$\frac{(p_0 - p)_{\text{KCl}}}{(p_0 - p)_{\text{mannite}}} = 1 + f_0 \quad (28)$$

where  $(p_0 - p)$  is the vapor-pressure lowering of the substance denoted by the subscript. In Table II, Col. 5 are given the values of  $f_0$  obtained by employing Equation 28. The agreement between these results and those in Col. 2 is good.

In order to carry the investigation somewhat further and to relate in a general way the osmotic coefficients from the freezing-point, vapor-pressure, and electromotive-force data with the reversible molal heat of dilution by water, it was thought advisable to compute the parameters of Equation 2 from the freezing-point and vapor-pressure data (Table II, Cols. 4 and 5) and then to make an approximate calculation of the reversible molal heat of dilution by water. Transposing and taking the log of both members of Equation 12c, we obtain

$$\log [1 - f_0 + \alpha''c] = \log \beta'' + m' \log c \quad (29)$$

where

$$\alpha'' = 2.3026\alpha'; \text{ and } \beta'' = \frac{4.065\beta'm'}{m' + 1}.$$

By plotting the  $\log [1 - f_0 + \alpha''c]$  against the  $\log c$ , a straight line should be obtained if  $\alpha''$  be assigned the correct value. From this plot  $\beta''$  and  $m'$  can readily be evaluated. In Fig. 3, the plots of the values obtained from

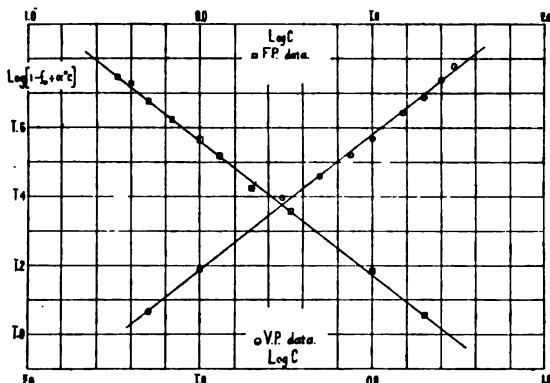


Fig. 3.

the freezing-point data (Table II, Col. 4) and vapor-pressure measurements (Table II, Col. 5) are shown. The values in parenthesis were omitted. In Table III are given the values of  $\alpha'$ ,  $\beta'$ , and  $m'$  obtained from these plots, and from the previous calculation.

TABLE III

VALUES FROM PLOTS

	F. p. (0°)	V. p. (20°)	E.m.f. (25°)
$\alpha'$ .....	0.052	0.068	0.070
$\beta'$ .....	0.277	0.292	0.292
$m'$ .....	0.387	0.395	0.397

The values from the freezing-point data conform very nearly to the straight line. The vapor-pressure data points do not fall so close to the straight. Lovelace, Frazer and Sease report that in the neighborhood of 0.4 to 0.8 *M*, the molecular vapor-pressure-lowering—concentration plot shows an irregularity not due to experimental error. Such an irregularity has never yet been found in electromotive-force measurements. For potassium chloride solutions, it would be observed between 1.5 and 2.0 *M* salt concentrations.

Calculation of the osmotic coefficients using the values of  $\alpha'$ ,  $\beta'$ , and  $m'$  in Table III will give values which increase with rise in temperature. From the fundamental thermodynamic equation

$$\frac{d\left(\ln \frac{p_0}{p}\right)}{dT} = \frac{\Delta \bar{H}}{RT^2} \quad (30)$$

and Equation 21, it follows that if the osmotic coefficient increases with

the temperature, then  $\frac{d\left(\ln \frac{p_0}{p}\right)}{dT}$  is positive, and  $\Delta \bar{H}$ , the partial molal heat content function of dilution is also positive. Hence, the reversible molal heat of dilution will be negative. This is in agreement with the data of

Stearn and Smith.<sup>15</sup> Further, the temperature coefficient  $\frac{d\left(\ln \frac{p_0}{p}\right)}{dT}$  decreases as the temperature rises so that in the neighborhood of from 20° to 25°, it is quite small. From the values of  $\alpha'$ ,  $\beta'$ , and  $m'$  in Table III,  $[i]$  was calculated and thence  $\ln \left(\frac{p_0}{p}\right)_{25}$  and  $\ln \left(\frac{p_0}{p}\right)_{20}$  were obtained by Equation 21. The temperature coefficient at 25° was taken as the difference  $\left[\ln \left(\frac{p_0}{p}\right)_{25} - \ln \left(\frac{p_0}{p}\right)_{20}\right]$  divided by 5. This mean coefficient is slightly higher than the true coefficient at 25° and, consequently, when  $\Delta H$  is calculated from this value, it should be slightly greater than the observed result. The final results of this calculation are given in Table IV.

TABLE IV  
FINAL RESULTS

$c$	$\ln \frac{p_0}{p} \Big _{25}$	$\ln \frac{p_0}{p} \Big _{20}$	$\frac{\left(\ln \frac{p_0}{p} \Big _{25} - \ln \frac{p_0}{p} \Big _{20}\right)}{5}$	$\frac{(-\Delta \bar{H})}{\text{Reversible molal heat of dilution (calories)}}$
1.000	0.03207	0.03198	0.000018	< - 3.2
2.000	0.06559	0.06523	0.000072	< - 12.7
3.000	0.1024	0.1013	0.00022	< - 38.8

Stearn and Smith obtained (-30.0) at 3.16  $M$ ; (-10.8) at 1.6  $M$ ; and (-3.2) at 0.8  $M$ . This is excellent agreement, and a splendid verification of the correctness of the original activity coefficients.

### 3. The Activity Coefficients of Sodium Chloride and Hydrochloric Acid Solutions.

The same method as used in the calculation of the activity coefficients of potassium chloride is employed with sodium chloride solutions, and need only be described briefly. The  $\log \left(\nu \lambda - \frac{\theta}{c}\right)$  was plotted against  $\log c$

<sup>15</sup> Stearn and Smith, *THIS JOURNAL*, **42**, 18 (1920).

using the freezing-point data of Harkins and Roberts,<sup>16</sup> and Flügel.<sup>8</sup> The plot is shown in Fig. 4 from which  $\alpha_1' = m' = 0.413$ ; and  $\beta_1' = 0.720$  which by Equation 27 gives  $\beta' = 0.288$ . Using these values in Equation 3, we obtain  $F_{a(s)} = 0.774$ . Assigning the value of 0.100 to  $\alpha'$  and employing Equation 2,  $F_{a(s)} = 0.792$ . This value will be accepted. The

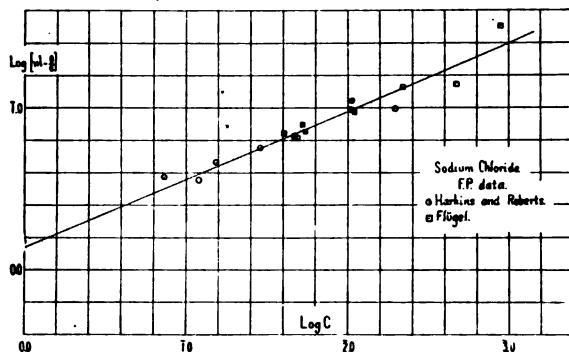


Fig. 4.

activity coefficients at concentrations above 0.1 *M* can now be calculated from the electromotive-force data of Allmand and Polack<sup>17</sup> and of Harned.<sup>18</sup> These are compiled in Table V.

TABLE V  
ACTIVITY COEFFICIENTS AT CONCENTRATIONS ABOVE 0.1 MOLAL

<i>c</i>	$F_a'$ (obs.) A. and P.	$F_a'$ (obs.) Harned	$F_a'$ (calc.) $\alpha' = 0.100$ $\beta' = 0.286$ $m' = 0.407$
0.1003	0.791	0.791	0.792
0.301	...	0.691	0.715
0.5034	0.686	0.671	0.674
1.022	0.653	0.664	0.651
2.000	...	0.693	0.679
3.196	0.735	...	0.726
6.12 (sat.)	1.019	...	1.033

Using the sedata,  $\log \left[ \frac{-\log F_a'}{c} + \alpha' \right]$  has been plotted against  $\log c$  (Fig. 5).

A straight line is obtained when  $\alpha' = 0.100$ . From this plot  $\beta' = 0.286$  and  $m' = 0.407$  which is again excellent agreement with the values of the same constants from freezing-point data. The values of  $\alpha'$ ,  $\beta'$ , and  $m'$  differ to a considerable extent from those computed by the same method from the results in Table XIV of Lewis and Randall's paper. From their data are obtained  $\alpha' = 0.140$ ;  $\beta' = 0.335$ ; and  $m' = 0.480$ .

<sup>16</sup> Harkins and Roberts, *THIS JOURNAL*, **38**, 2676 (1916).

<sup>17</sup> Allmand and Polack, *J. Chem. Soc.*, **115**, 1020 (1919).

<sup>18</sup> Harned, *THIS JOURNAL*, **40**, 1462 (1918).

Fig. 5 also contains the plot of  $\log \left[ \frac{-\log F_{a'}}{c} + \alpha' \right]$  against  $\log c$  for hydrochloric acid solutions. The activity data were taken from the electromotive-force data of Ellis,<sup>19</sup> and Noyes and Ellis.<sup>20</sup> From this plot,  $\alpha' = 0.200$ ;  $\beta' = 0.286$ ; and  $m' = 0.434$ .

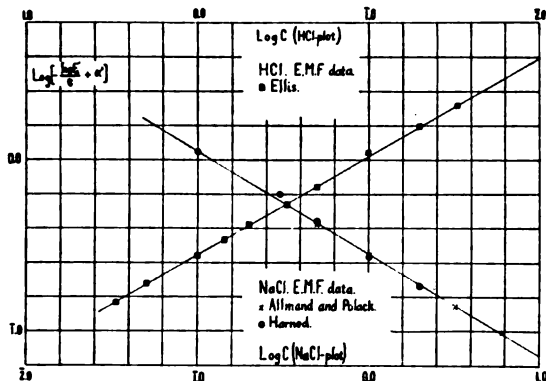


Fig. 5.

Table VI contains a summary of the values for the parameters  $\alpha'$ ,  $\beta'$ , and  $m'$  obtained in this paper and the values of  $\alpha$ ,  $\beta$ , and  $m$  computed therefrom for the individual ions on the assumption that  $F_{a_K} = F_{a_{Cl}}$  and that the ions act independently.<sup>3</sup> These values for the independent ion-activity coefficients are to be regarded as an approximation and are subject to change as a result of further accumulation of evidence.

TABLE VI  
SUMMARY

	KCl	NaCl	HCl
$\alpha'$ .....	0.070	0.100	0.200
$\beta'$ .....	0.292	0.286	0.288
$m'$ .....	0.396	0.407	0.434
	$K^+ = Cl^-$	$Na^+$	$H^+$
$\alpha$ .....	0.070	0.130	0.330
$\beta$ .....	0.292	0.280	0.284
$m$ .....	0.396	0.417	0.471

These values substituted in Equations 12, 20 and 22 will give numerical equations by means of which the vapor pressures and osmotic pressures of these solutions at 25° may be accurately calculated.

#### 4. Calculation of the Colligative Properties of Other Electrolytes.

The values of  $\alpha'$ ,  $\beta'$ , and  $m'$  for the different electrolytes in Table XIV in Lewis and Randall's paper have been obtained by the same method as

<sup>19</sup> Ellis, *THIS JOURNAL*, **38**, 737(1916).

<sup>20</sup> Noyes and Ellis, *ibid.*, **39**, 2532(1917).

above and compiled in Table VII. In the second column are given the ranges of concentration over which the values of the constants may be regarded as valid. The values of these parameters with the possible exception of lithium chloride and hydrochloric acid are not as accurate as the values in Table VI and are subject at any time to revision.

TABLE VII  
VALUES CALCULATED FROM LEWIS AND RANDALL'S PAPER

Electrolyte	Range of validity	$\alpha'$	$\beta'$	$m'$
LiCl (25°).....	0.01-3	0.200	0.323	0.463
KNO <sub>3</sub> .....	0.01-0.1	...	0.497	0.558
AgNO <sub>3</sub> .....	0.01-5	...	0.406	0.470
KIO <sub>3</sub> , NaIO <sub>3</sub> .....	0.01-0.1	...	0.469	0.468
BaCl <sub>2</sub> .....	0.01-0.1	...	0.643	0.327
CdCl <sub>2</sub> (25°).....	0.01-0.1	...	1.901	0.441
K <sub>2</sub> SO <sub>4</sub> .....	0.01-0.1	...	0.873	0.363
H <sub>2</sub> SO <sub>4</sub> .....	0.01-3	0.470	1.365	0.402
La(NO <sub>3</sub> ) <sub>3</sub> .....	0.01-0.2	...	0.933	0.286
MgSO <sub>4</sub> .....	0.01-0.1	...	1.496	0.290
CdSO <sub>4</sub> .....	0.01-0.2	...	1.611	0.306
CuSO <sub>4</sub> .....	0.01-0.5	...	1.496	0.290

By using Equation 12 or 16, accurate values of the vapor pressures of these solutions may be computed; and by using Equation 22 the osmotic pressures may be obtained.

### 5. The Limit of Validity of Equation 2.

In all cases yet studied, Equation 2 has been found to hold within the present experimental error throughout the entire concentration range of available data with the exception of sulfuric and hydrochloric acids. Lewis

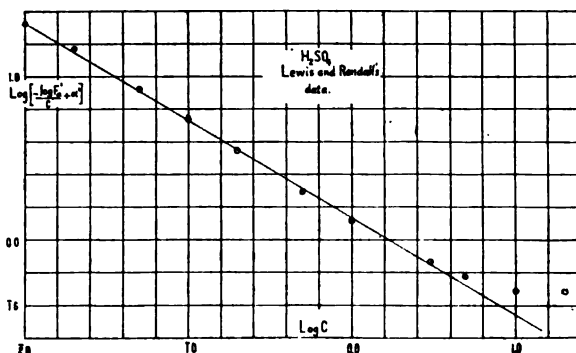


Fig. 6.

and Randall have obtained the activity coefficients of sulfuric acid from 0.01 to 20 molal. The plot of  $\log \left[ \frac{\log F_a'}{c} + \alpha' \right]$  against  $\log c$  is shown

in Fig. 6 whence can be seen that the curve departs from a straight line above 3 *M* concentration.

### Summary.

1. On the basis of an empirical equation

$$\log F_a' = \alpha'c - \beta'c^m \quad (2)$$

which relates the activity coefficient of an electrolyte with the molal concentration at a given temperature, and Duhem's equation, equations are derived for calculating the vapor pressures of solutions at this temperature.

2. A rigorous test was made of the validity of Equation 2. It was found to hold for all electrolytes throughout the concentration ranges where available data were examined with the exception of sulfuric and hydrochloric acids. In these cases it holds up to 3 *M* concentration.

3. A very careful and exhaustive study of the activity coefficients of potassium chloride solutions has been made.

4. A careful but less exhaustive study of the activity coefficients of sodium chloride solutions and hydrochloric acid solutions has been made.

5. Values of the parameters of Equation 2 obtained for the above 3 and numerous other electrolytes have been collected and tabulated, from which the vapor pressures and osmotic pressures of their solutions may be calculated.

It is thought that the equation and method here employed, although empirical and an approximation will prove useful in testing the consistency and accuracy of activity data and also will prove of some service in organizing the colligative data of concentrated solutions.

PHILADELPHIA, PENNSYLVANIA.

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[CONTRIBUTION FROM THE BUREAU OF STANDARDS, U. S. DEPARTMENT OF COMMERCE.]

## A SIMPLE THEORY OF THE NEPHELOMETER.<sup>1</sup>

By P. V. WELLS.

Received November 9, 1921.

In recent years several instruments have been developed using as a measuring criterion the light diffusely reflected and transmitted by suspensions, and variously called turbidimeters, tyndallmeters and nephelometers. At present there is on the market the Kober nephelometer<sup>2</sup> (a development of the modification by Richards and Wells of the Dubosq colorimeter) which measures the ratio of the depths of two suspensions of equal brightness either by diffuse reflection or transmission.

These instruments are used to obtain information about the suspension

<sup>1</sup> Published by permission of the Director of the Bureau of Standards.

<sup>2</sup> Made by Klett Mfg. Co., 202 E. 46th St., New York City.



The readings can be correlated with the concentration, fineness, and other properties of the suspended matter in a purely empirical way, but a theoretical basis for such experimental studies is preferable. Unfortunately the optics of turbid media are extremely complicated, but simple considerations are sufficient to show the general trend of the phenomena.

### Diffuse Transmission.

In attempting to derive laws for the tyndallmeter,<sup>3</sup> the theory of the late Lord Rayleigh of scattering of light by particles small compared with the wave-length of light, which explains the blue color of the sky and the hues of the sunset, has been applied to dispersoids without much regard to the size of particles; but the particles of suspensions are large compared with the wave-length of light, the Tyndall beam is whitish instead of deep blue so that the law of Rayleigh does not apply. In fact, the appearance of suspensions is due largely to the effects of diffuse reflection. Consider first diffuse transmission. Ignoring the question of directional distribution in the light flux, assume simply that the same fraction  $-dI/I$  of the light is lost in each thickness  $dx$  of the suspension traversed. That is

$$-dI = \alpha I dx. \quad (1)$$

The coefficient  $\alpha$  depends upon the concentration and size, distribution of the particles, the optical properties of the dispersoid, etc., but it is assumed not to vary with the depth  $x$ . Integrating, the transmission  $T$  of a thickness  $x$ , or ratio of transmitted to incident light, is

$$= T \exp.(-\alpha x). \quad (2)$$

The coefficient  $\alpha$  can be taken to include the true absorption of the suspending medium, as well as the obstruction of the light by the particles in its path, for neither varies with the depth. But a small fraction of the obstructed light gets back into the original beam after multiple reflections in all directions among the particles, and while this is constant for any given direction, more directions contribute as the light becomes more and more diffused. This secondary reflection coefficient would therefore be expected to increase with the depth, approaching a constant  $\gamma$  when the light becomes perfectly diffused. These conditions are satisfied by the coefficient  $\gamma [1 - \exp. (-\frac{\beta x}{\gamma})]$ , where  $\beta$  is a constant, so that (1) may be improved by taking

$$\frac{1}{I} \frac{dI}{dx} = \gamma - \alpha - \gamma \exp. \left( -\frac{\beta x}{\gamma} \right). \quad (3)$$

Integrating, as before, the transmission is

$$T = \exp. \left\{ (\gamma - \alpha)x - \frac{\gamma^2}{\beta} \left[ 1 - \exp. \left( -\frac{\beta x}{\gamma} \right) \right] \right\}. \quad (4)$$

<sup>3</sup> W. Mecklenburg, *Kolloid Z.*, 15, 149 (1914); 16, 97 (1915).

Since the transmission must vanish for great depths,  $\gamma$  must be less than  $\alpha$ , that is, only a small part of the diffusely reflected light ever gets back into the original beam. Equation 4 is too complicated to be useful, but when  $\beta x$  is small compared with  $\gamma$  we have the power series  $\exp.(-\frac{\beta x}{\gamma}) = 1 - \frac{\beta}{\gamma} x + \frac{1}{2} (\frac{\beta}{\gamma} x)^2 \dots$ , so that (4) gives

$$T = \exp. \left[ -\alpha x + \frac{1}{2} \beta x^2 \dots \right], \quad (5)$$

neglecting higher powers. Thus, the effect of multiple reflection drops out completely to a first approximation if it varies slowly with the depth, and the fractional error in Equation 2 is  $\frac{1}{2} \beta x^2$  for moderate depths.

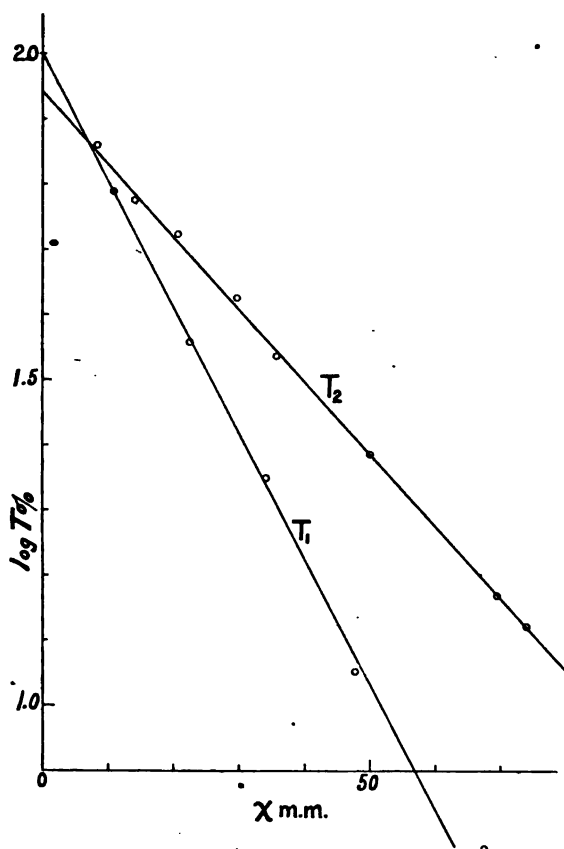


Fig. 1.—Diffuse transmission.

This relation was tested experimentally on a Kober nephelometer in the case of 2 silica suspensions, one containing a concentration of about  $5 \times 10^{-5}$  g. per cc. (50 parts per million) of material which remained in

suspension 20 hours, the other about  $12 \times 15^{-5}$  g./cc. (120 p. p. m.) of larger particles. The latter will be designated by the subscript 1 ( $T_1$ ,  $\alpha_1$ ,  $x_1$ , etc.), the former by the subscript 2. Two nicol prisms were mounted on one side of the instrument, to measure the transmission of the sample on the other side. In logarithmic form, Equation 5 is

$$2.3 \log T = -\alpha x + \frac{1}{2}\beta x^2 \quad (6)$$

so that if  $\beta$  is small, the logarithm of the transmission should be nearly linear with the depth. This is confirmed by the results in Fig. 1. The initial value of  $\log T_2$  (1.942) is probably due to imperfect matching at  $x_2=0$ .

A computation of the value of  $\beta$  after determining  $\alpha$  graphically, is given in Table I, neglecting transmissions too near 100%, which are vitiated by lack of precision. Thus over ranges of 50 mm. Equation 5 holds well within the limit of experimental error,<sup>4</sup> the two samples giving, respectively,

$$\begin{aligned} T_1 &= \exp. [-0.0475x_1 + 0.000096x_1^2] \\ T_2 &= \exp. [-0.0350x_2 + 0.000153x_2^2]. \end{aligned} \quad (7)$$

There is even an indication in the experimental results that the sign of the term in  $x^2$  is again negative, as would be expected from the negative exponential expansion; but the precision is not sufficient to give this much weight.

TABLE I  
DIFFUSE TRANSMISSION  
Percentage transmission  
 $T_1$

Depth $x_1$ mm.	Obs.	Calc.	$\beta_1 \times 10^6$ ( $\alpha_1 = .0475$ )
10.8	60.7	60.5	22
22.4	35.9	36.2	16
34.1	22.3	22.1	21
47.4	12.7	12.8	18
68.1	6.1	6.1	19

Mean  $\beta_1 = .000192$

$x_2$	$T_2$		$\beta_2 \times 10^6$ ( $\alpha_2 = .035$ )
20.6	52.6	51.8	37
29.8	42.2	40.3	40
35.7	34.3	34.7	28
50.0	24.2	25.4	27
69.4	16.6	18.4	26
74.0	14.9	17.3	25

Mean  $\beta_2 = .00305$

<sup>4</sup> Some difficulty was experienced in the photometric work because the nicols did not give a perfectly flat field.

## Diffuse Reflection.

Now consider a column of the suspension viewed in the direction of its depth  $x$ , but uniformly illuminated from the side by a parallel beam of intensity,  $I_0$ . The portion  $dI$  of the reflected intensity coming from the layer  $dx$  at the depth  $x$  is

$$dI = kI_0 \exp. (-\alpha x) dx, \quad (8)$$

the exponential representing the attenuation in transmission. The coefficient  $k$  is probably more nearly constant than  $\alpha$ , because of the similarity in the conditions at each layer. Integrating (8), the reflection  $R$  of a thickness,  $x$ , or ratio of reflected and incident intensities, is thus

$$R = m(1 - T) \quad (9)$$

where  $m = k/\alpha$ . This is a very simple expression for the diffuse reflection, giving its relation to the diffuse transmission. It is obvious from (9) that the reflection  $R$  increases toward the limiting value  $m$  with increasing thickness  $x$ , because the transmission  $T$  decreases exponentially from unity toward zero, as shown in (2), with increasing depth.

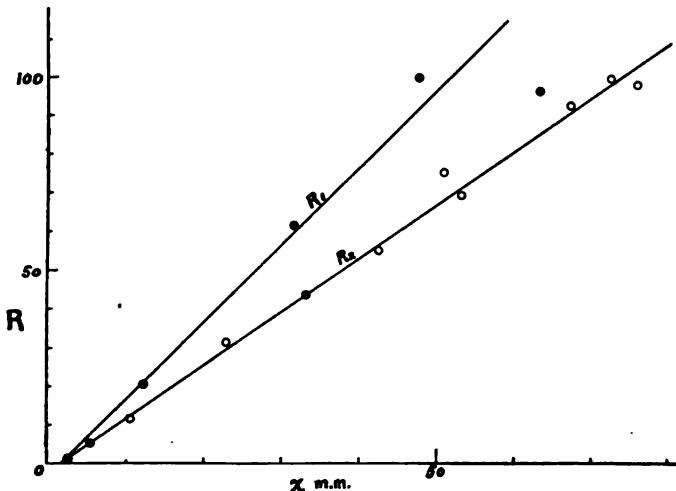


Fig. 2.—Diffuse reflection.

The observed laws of reflection for the 2 silica suspensions before mentioned are shown in Fig. 2. Within the rather large limits of experimental error the reflections are distinctly linear with the depth even to depths of 75 mm. This does not agree with Equation 9; but that equation is deduced on the assumption that the illumination  $I_0$  is uniform. This was tested on the Kober nephelometer. A ground glass diffusion screen, placed upon the cup carriage, increased in brightness approximately linearly with the depth, so that the illumination  $I_0'$  is more nearly

$$I_0' = I_0(1 + \omega x) \quad (10)$$

where  $\omega = 0.045$ .

Introducing this into (8), the reflection becomes, in place of (9), to a second approximation in  $\alpha x$ ,

$$R = kx \left[ 1 - \frac{1}{2}(\alpha - \omega)x \right] \quad (11)$$

so that the effect of the increase in illumination with the depth is to compensate for the attenuation in transmission. The values of the coefficient in the second term for the 2 silica suspensions are, respectively,  $+0.001$  and  $-0.005$ . The latter is too large to agree with the results of Fig. 2, but the  $\beta$ -term in (5) has been neglected in deducing (9) and (11).

From these observations it is evident that the law of reflection, as read on the nephelometer, is a fixed function of the depth only so long as the source of light (a concentrated filament lamp) and the collimating lens remain fixed in position, and that this law must be determined empirically. Moreover, there is no simple way of adjusting these parts, when once moved, as there is in the case of transmission. Empirical calibration curves must therefore be frequently redetermined for reliable results.

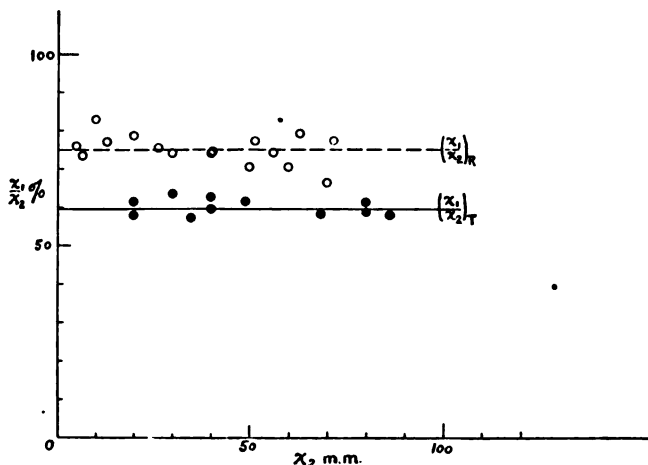


Fig. 3.—Depth ratios.

In the Kober nephelometer 2 suspensions are compared for diffuse transmission, using the opaque cups with transparent bottoms, by varying the depth  $x_1$  of one sample until it matches the other in transmission. It follows from the small values of  $\beta$  in the expression (5) for the transmission, that the ratio of the depths  $(x_1/x_2)_T$  of equi-transmitting layers is very nearly constant. The depth ratio  $(x_1/x_2)_R$  for equi-reflecting layers is also approximately constant, because the reflections are nearly linear with the depth. This was tested directly on the nephelometer,

with the results shown in Fig. 3. The average deviation of a single determination from the mean of 11 determinations of the transmission depth ratio was 1.9%; while the a. d. of 16 determinations of the reflection depth ratio was 3%. These results show that both ratios are very nearly constant with changes in the depth.

### Concentration and Size of Particle.

In order to measure the concentration of the dispersed phase upon the nephelometer, relations between this quantity and the characteristic constants  $\alpha$ ,  $k$ , and  $m$  must be known. Confining our attention to *uniform suspensions* (the simplest case), in which all the particles are identical, their size may be specified by a linear dimension,  $d$ . For small depths the resultant reflection is due to light reflected from the surfaces of the particles, so that one would expect the constant  $k$  to be nearly independent of the wave-length,<sup>5</sup> and to be proportional to the total surface of the particles per unit volume. This gives

$$k = k' \frac{C}{d} \quad (12)$$

where  $C$  is the concentration. The constant  $k'$  depends merely upon the arrangement of the particles in space, upon the refractive indices of the two phases, the form of the interfaces, etc.

Assuming Equation 12 it is evident that the diffuse reflection could be used as a measure either of the concentration or of the size of particle of a uniform suspension provided only that one or the other of these properties is known or is kept fixed. This is not difficult in the case of the concentration. But as suspensions are rarely in true equilibrium,<sup>6</sup> the particles are continually coalescing to form larger aggregates, especially at high concentrations. For stable uniform suspensions with the same constants ( $k_1' = k_2'$ ), (11) and (12) give for the concentration ratio ( $C_1/C_2$ ) of equi-reflecting layers of small depth

$$\frac{C_1}{C_2} = \frac{d_1}{d_2} \left( \frac{x_2}{x_1} \right). \quad (13)$$

The same relation holds for moderate depths, if the concentration  $C_2$ , size of particle  $d_2$ , and depth  $x_2$  of one suspension be kept fixed. This is what is done in practise. A standard of known concentration,  $C_2$ , is placed in one cup at a fixed depth,  $x_2$ . It is then compared with known dilutions,  $C_1$  giving depths  $x_1$ . Assuming the size of particle to remain constant on dilution, this factor drops out. The resulting calibration curve may be called the *dilution law* (by reflection) of the instrument for this suspension.

<sup>5</sup> The finer a powder is ground, the less color it shows.

<sup>6</sup> Tolman has shown that only uniform dispersoids can be in complete thermodynamic equilibrium. *THIS JOURNAL*, 35, 317 (1913).

Some reflection dilution laws are given by Kober<sup>7</sup> in his article on nephelometry. He finds his results to be well fitted by the formula

$$\left(\frac{x_1}{x_2}\right)_R = \frac{C_2}{C_1} \left[ 1 + k \left( 1 - \frac{C_2}{C_1} \right) \right] \quad (14)$$

This is a single-constant form of second approximation. Another single-constant formula of a somewhat more flexible type is

$$\frac{C_1}{C_2} = \left( \frac{x_2}{x_1} \right)^\xi \quad (15)$$

This gives for Kober's results on ammonia  $\xi = 0.9342$ , very nearly unity, and agrees to 0.1%. The constant  $\xi$  is most simply determined graphically. The logarithms of the depths and concentrations are plotted, and the slope of the resulting straight line is  $\xi$ . An approximate form of (15) is very convenient for the slide-rule, and suffices for ratios near unity. When  $\delta = 1 - \xi$  is small

$$\frac{C_1}{C_2} = \frac{x_2}{x_1} \left[ 1 + \delta \left( 1 - \frac{x_2}{x_1} \right) \right] \quad (16)$$

This is of the same form as Kober's but with the depth ratio as the independent variable, which is more convenient. For example, in Kober's data ( $x_1 = 29.2$ ,  $x_2 = 20$ ,  $C_1/C_2 = 0.7$ ), Equation 16 gives, since  $\delta = 1 - 0.934 = 0.066$ ,  $C_1/C_2 = .685(1 + 0.066 \times 0.315) = 0.700$  which is exact to 0.1%. The error at  $C_1/C_2 = 0.5$  is 1.4%. A single determination (10 readings) is seldom precise to 0.5%, and may contain much larger inaccuracies, due to settling, imperfect washing, bubbles, etc.<sup>8</sup> The constant  $\delta$  is easily

obtained directly from observed values of  $\left( \frac{C_1 x_1 / C_2 x_2 - 1}{1 - x_2 / x_1} \right)$

The departure of (15) from the first approximation (13) is probably due to secondary optical effects, but a slight breaking up of the particles on dilution would explain observed values of the exponent  $\xi$  in (15) less than unity. The known difficulty of producing stable suspensions, and the tendency of the particles to coalesce at high concentrations renders this explanation not altogether improbable. Equation 13 also indicates that the ratio of the sizes of particle of two uniform suspensions of the same material and concentration is equal to the depth ratio at equal reflection.

The transmission constant  $\alpha$  is the ratio of the reflection constants  $k$

<sup>7</sup> Kober, *J. Ind. Eng. Chem.*, **10**, 562 (1918).

<sup>8</sup> The mean of 6 determinations at depths between 10 and 30 mm. on the Kober Nephelometer under good conditions gave for the average deviation of a single observation from means of ten, 2.1%. This corresponds to a probable error in the mean of 0.56%; but two consecutive determinations on the same suspension, one with the left cup fixed at 10 mm., the other with the right, gave depth ratios differing by 2%.

and  $m$ . Now it seems reasonable to assume that  $m$  is independent of the concentration and size of particle. Then (12) gives

$$\alpha = \alpha' \frac{C}{d} \quad (17)$$

where  $\alpha' = k'/m$  is a constant, independent of the depth, concentration, and size of particle. If this constant is the same for 2 suspensions, (2) and (17) give at equal transmission

$$\frac{d_1}{d_2} = \frac{C_1}{C_2} \left( \frac{x_1}{x_2} \right)^{\xi}, \quad (18)$$

a first approximation of exactly the same form as (13) for reflections. Hence the depth ratio on dilution should be approximately the same, whether determined by reflection or by transmission. This was verified on the Kober nephelometer, using the silica suspension (No.1), before mentioned. The concentration ratio was measured at six dilutions from 1 to 4, and the exponent  $\xi$  in (15) determined for the best straight line by Pearson's method of moments (in this case the same as the method of least squares). By reflection the value of  $\xi$  was 0.924, by transmission 0.904, a very close agreement. This indicates that the reflection constant  $m$  is practically independent of the concentration, and again favors the supposition that the particles break up on dilution.

The depth ratio, either by reflection or by transmission, can be used to measure the ratio of size of particle ( $d_1/d_2$ ) in two uniform suspensions with the same constant ( $k'$  or  $\alpha'$ ) and of known concentrations. For Equations 13 and 18 state that the particle size is in the same ratio as the depths.<sup>9</sup> But while finer suspensions transmit less light per unit depth than do coarser ones of the same material and concentration, more light is diffusely reflected by the finer suspensions.

### Summary.

The fact that the depth ratios by reflection and by transmission are equal might lead one to think that either method could be used with the same result. But this is so only in an intermediate range of concentrations. For extremely dilute suspensions, say less than  $10^{-4}$  g. per cc., the transmissions are quite insensitive, while the reflection measurement remains sensitive right down to the threshold of vision. By increasing the incident intensity the present Lord Rayleigh has been able to measure the light scattered by gas molecules. On the other hand, for very turbid suspensions the transmission probably follows less complicated laws. Although masses in suspension much too small to be detected by the most delicate balance can be easily measured in a Tyndall beam, the precision of such a

<sup>9</sup> The depth ratio by transmission has been utilized by Bleininger and Pendergast in classifying clay suspensions according to fineness (to be published in the *J. Am. Ceramic Soc.*).



measurement can never exceed that of the best photometry, that is, about 0.2%. For sensitive and rapid work it takes its place with other volumetric methods.

The phenomena of diffuse reflection and transmission are much more complicated than is here represented, many secondary effects occurring that cannot be neglected. The experimental dilution law is an example of the departures which are to be expected. Moreover, the particles are usually distributed in size, and must be studied statistically. But the simple theory represents the general march of the phenomena,<sup>10</sup> and it may serve as a point of departure for experimental investigations.

WASHINGTON, D. C.

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[CONTRIBUTION FROM THE GATES CHEMICAL LABORATORY, CALIFORNIA INSTITUTE OF TECHNOLOGY. NO. 9.]

## THE CRYSTAL STRUCTURES OF POTASSIUM AND AMMONIUM CHLOROSTANNATES.

By ROSCOE G. DICKINSON.<sup>1</sup>

Received November 9, 1921.

### 1. Introduction.

There is a large group of substances of the type  $R_2MHI_6$ , where R is potassium, rubidium, cesium, or ammonium; M is one of the platinum metals or tin, antimony, selenium, tellurium or lead; and HI is one of the halogens, chlorine, bromine or iodine. Although few members of this group have been thoroughly studied crystallographically, many of them are apparently isomorphous<sup>2</sup> and belong to the cubic system. They crystallize chiefly in octahedra, and show a very good octahedral cleavage. There are in addition other salts, such as  $K_2SiF_6$ , which have similar cubic modifications.

Since the crystal structures of these salts presumably differ only in detail, the determination of the structures of one or two of them by means of X-rays should furnish the key to the group as a whole.<sup>3a</sup> Potassium chlorostannate ( $K_2SnCl_6$ ) was chosen for the investigation, since definite

<sup>10</sup> See, for example, R. C. Tolman and others, *THIS JOURNAL*, **41**, 575 (1919). Tolman's tyndallmeter measures the diffuse reflection of a single sample at right angles to the incident beam. The (fixed) depth is small, so that Equations 11 and 12 apply. The diameter of particles is found to be fairly linear with the concentration over considerable ranges.

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<sup>2</sup> Groth, "Chemische Krystallographie," Engelmann, Leipzig, 1906, vol. 1, p. 467.

<sup>3a</sup> Since the submission of this paper for publication the determination of the structure of another crystal of this series has been published by Wyckoff and Posnjak (*THIS JOURNAL*, **43**, 2292 (1921)). Their results are in entire agreement with those described here, and afford an interesting comparison of interatomic distances.

crystallographic information<sup>3</sup> is available, and since sufficiently good crystals can be prepared. Ammonium chlorostannate  $((\text{NH}_4)_2\text{SnCl}_6)$  was also found to give good crystals, and it was studied to confirm the work on the potassium salt.

All of the X-ray data were obtained photographically. Two methods of experimentation were used: (1) characteristic X-rays were reflected from single faces of the crystals, and line spectra obtained; (2) general radiation was passed perpendicularly through slips of crystal cut at a small angle with an important face, and unsymmetrical Laue photographs obtained.

## II. Spectral Photographs of Potassium Chlorostannate.

The method used in obtaining the line spectra was similar to that used by Wyckoff,<sup>4</sup> in that the X-rays were allowed to fall simultaneously on the crystal under investigation and on a reference crystal, the two crystals being mounted one above the other on a holder oscillating about an axis in the plane of the crystal faces. The rays reflected from both crystals were registered on a photographic plate placed perpendicularly to the incident beam. The K radiation from a rhodium target was used, and the lines measured were  $\beta$  and  $\alpha_1$ , (wave lengths<sup>5</sup> 0.5453 and 0.6121 Å., respectively), and for reference, the (100) face of calcite was used ( $d = 3.028 \text{ Å.}$ ). Spectra of more than one order appeared on the photograph; and since a rough comparison of the intensities was useful in the present case, it was attempted to make the intensities reliable by choosing a sufficiently large crystal, using a narrow slit, grinding the face carefully, and oscillating with uniform velocity.

The crystals of potassium chlorostannate were prepared either by the slow evaporation or by slow cooling of a solution of stannic chloride and potassium chloride to which a small amount of hydrochloric acid was added. Two density determinations each gave the value 2.71 g./cc. The values quoted by Groth are 2.687 and 2.700.

The photographs were treated in the following manner. First, the angle of reflection,  $\theta$ , of each calcite line was calculated, using the equation  $n\lambda = 2d \sin \theta$ , in which  $\lambda$  and  $d$  are known. From these the values of  $\tan 2\theta$  were obtained. Then an arbitrary straight line was fixed on the photograph parallel to the spectral lines. The distance of each spectral line from the arbitrary line was measured. This distance is evidently a linear function of  $\tan 2\theta$ . The measured distances for calcite were plotted against the corresponding values of  $\tan 2\theta$  and a straight line was drawn. From this graph the values of  $\tan 2\theta$  for the crystal under investigation were immediately taken. It was thus possible to measure the angles of reflection

<sup>3</sup> Ref. 2, p. 488.

<sup>4</sup> Wyckoff, *THIS JOURNAL*, 42, 1102 (1920).

<sup>5</sup> Duane, *Nat. Research Council, Bull.* 1, No. 6 (1920).

without a knowledge of either the distance of the plate or the center of the central image.

TABLE I  
REFLECTION DATA FOR POTASSIUM CHLOROSTANNATE

Plane	Line	Observed angle of reflection	$\frac{n^2}{m}$	$n$	$d_{100}$	Intensity
(110)	$\beta$	4°26'	2.01	2	9.98	
	$\alpha_1$	4 59	2.01	..	9.96	Medium
	$\beta$	8 55	....	4	9.95	
	$\alpha_1$	10 3	....	..	9.92	Strong
(111)	$\beta$	2 41	0.242	1	(10.1)	
	$\alpha_1$	3 2	0.248	..	(10.0)	Strong
	$\beta$	5 26	....	2	9.97	
	$\alpha_1$	6 6	....	..	9.97	Strong
	$\beta$	8 10	....	3	9.97	
	$\alpha_1$	9 13	....	..	9.93	Weak
	$\beta$	10 56	....	4	9.96	
	$\alpha_1$	12 20	....	..	9.93	Medium
				Mean	9.96 Å.	

Calc. from density 9.99

The angles of reflection obtained in this way are given in the third column of Table I. The order of each spectrum is in the first instance unknown. If the crystal be regarded as built up by the repetition on a simple cubic lattice of a unit structure containing  $m$  molecules of  $K_2SnCl_6$

then  $\frac{n^2}{m} = \left( \frac{2 \sin \theta}{\lambda \sqrt{h^2 + k^2 + l^2}} \right)^2 \frac{M}{N\rho}$  where  $M$  is the molecular weight,  $\rho$  the

density, and  $N$  the Avogadro number,<sup>6</sup>  $6.062 \times 10^{23}$ . For the first spectrum from the (110) face the value of  $n^2/m$  is evidently 2, and for that from the (111) face it is  $1/4$ . Since  $n$  is an integer in each case and  $m$  is presumably a submultiple of 192, there are evidently either 4 or 32 molecules per unit of structure. On the simpler assumption of 4 molecules, the first spectrum from (110) is of the second order, and the first from (111) is of the first order. The repetition distance  $d_{100}$  of the lattice may now be

calculated from the formula  $d_{100} = \frac{n\lambda \sqrt{h^2 + k^2 + l^2}}{2 \sin \theta}$ . The values so

obtained are given in the sixth column.

### III. Application of the Theory of Space Groups.

The theory of space groups will now be applied to the foregoing data, taking the point of view outlined by Wyckoff.<sup>7</sup>

There appears to be no crystallographic evidence that the symmetry of potassium chlorostannate is less than that of the holohedry of the cubic

<sup>6</sup> Millikan, *Proc. Nat. Acad. Sci.*, 3, 314 (1917).

<sup>7</sup> Wyckoff, *Am. J. Sci.*, 1, 127 and 138 (1921).

system. However, there is not much positive evidence of holohedry. As no evidence of dissymmetry was observed in the Laue photographs described below, the atomic arrangement probably has a symmetry isomorphous with that of one of the point-groups<sup>8</sup>  $T^d$ ,  $O$ , or  $O^h$ ; a consideration of the symmetry alone of the photographs takes us no further than this, since apparently all crystals behave toward X-rays as if they possessed a center of symmetry.

It will be assumed that all of the potassium atoms are equivalent, likewise all of the tin atoms. From a chemical point of view, it might seem reasonable to assume that, among the chlorine atoms, two are not equivalent to the other four. Then since there are either 4 or 32  $K_2SnCl_6$  groups per unit of structure, a space group is required which gives either 8, 4, 8, and 16, equivalent positions per unit of structure, or 64, 32, 64, and 128 such positions. But, according to the tabular summary given by Niggli,<sup>9</sup> no cubic space group has this property. If the assumption is made that all of the chlorine atoms are equivalent, the proper space group should give either 8, 4, and 24 positions, or 64, 32, and 192 positions. The same table indicates that the space groups  $O^2$ ,  $O^3$ ,  $O^6$ ,  $O^7$ , and  $O_h^4$  and  $O_h^8$  are possible with 4  $K_2SnCl_6$  groups per unit, and  $O_h^8$ , with 32 per unit.

The coordinates defining all of these arrangements need not be given. It may be said that those derived from the space groups  $O^2$ ,  $O^6$ ,  $O^7$ , and  $O_h^4$  make it difficult to account for the fact that in the Laue photographs described below, first orders of reflection do not appear in planes having any even index. The more complicated arrangement derivable from  $O_h^8$  has been discarded for a similar reason. The two types of arrangement derived from  $O^8$  are identical with those from  $O_h^8$ .

In either arrangement derived from  $O_h^8$  the coordinates<sup>10</sup> of the potassium and tin atoms, placing  $d_{100}$  equal to unity, are as follows.<sup>11</sup>

K:  $(\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$   $(\frac{1}{4}, \frac{3}{4}, \frac{3}{4})$   $(\frac{3}{4}, \frac{1}{4}, \frac{3}{4})$   $(\frac{3}{4}, \frac{3}{4}, \frac{1}{4})$   $(\frac{3}{4}, \frac{3}{4}, \frac{3}{4})$   $(\frac{1}{4}, \frac{1}{4}, \frac{3}{4})$   $(\frac{3}{4}, \frac{1}{4}, \frac{1}{4})$   $(\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$ .

Sn:  $(0, 0, 0)$   $(\frac{1}{2}, \frac{1}{2}, 0)$   $(\frac{1}{2}, 0, \frac{1}{2})$   $(0, \frac{1}{2}, \frac{1}{2})$ .

There are two possible arrangements for the chlorine atoms, as follows.

Arrangement I. Cl:  $(\frac{1}{4}, \frac{1}{4}, 0)$   $(\frac{1}{4}, \frac{3}{4}, 0)$   $(\frac{3}{4}, \frac{1}{4}, 0)$   $(\frac{3}{4}, \frac{3}{4}, 0)$   $(\frac{1}{4}, \frac{1}{4}, \frac{1}{2})$   $(\frac{1}{4}, \frac{3}{4}, \frac{1}{2})$   $(\frac{3}{4}, \frac{1}{4}, \frac{1}{2})$   $(\frac{3}{4}, \frac{3}{4}, \frac{1}{2})$   $(0, \frac{1}{4}, \frac{1}{4})$   $(0, \frac{1}{4}, \frac{3}{4})$   $(0, \frac{3}{4}, \frac{1}{4})$   $(0, \frac{3}{4}, \frac{3}{4})$   $(\frac{1}{2}, \frac{3}{4}, \frac{1}{4})$   $(\frac{1}{2}, \frac{3}{4}, \frac{3}{4})$   $(\frac{1}{2}, \frac{1}{4}, \frac{1}{4})$   $(\frac{1}{2}, \frac{1}{4}, \frac{3}{4})$   $(\frac{1}{4}, 0, \frac{1}{4})$   $(\frac{3}{4}, 0, \frac{1}{4})$   $(\frac{1}{4}, 0, \frac{3}{4})$   $(\frac{3}{4}, 0, \frac{3}{4})$   $(\frac{1}{4}, \frac{1}{2}, \frac{3}{4})$   $(\frac{3}{4}, \frac{1}{2}, \frac{3}{4})$   $(\frac{1}{4}, \frac{1}{2}, \frac{1}{4})$   $(\frac{3}{4}, \frac{1}{2}, \frac{1}{4})$ .

<sup>8</sup>Schönflies, "Krystallsysteme und Krystallstructure," Teubner, Leipzig, 1891, p. 229.

<sup>9</sup>Niggli, "Geometrische Krystallographie des Diskontinuums," Gebrüder Borntraeger, Leipzig, 1919, p. 40; also *Physik. Z.*, 19, 229 (1918).

<sup>10</sup>The coordinates for these special cases were derived from those for the general case given by Schönflies (Ref. 8, p. 549).

<sup>11</sup>The tin atoms might be placed at  $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$   $(\frac{1}{2}, 0, 0)$   $(0, \frac{1}{2}, 0)$   $(0, 0, \frac{1}{2})$ ; but the resulting arrangement would, with a suitable alteration in the value of  $u$  in Case II, be identical with that given.

Arrangement II. Cl: (u, 0, 0) ( $\bar{u}$ , 0, 0) ( $\frac{1}{2} + u$ ,  $\frac{1}{2}$ , 0) ( $\frac{1}{2} - u$ ,  $\frac{1}{2}$ , 0) ( $\frac{1}{2} + u$ , 0,  $\frac{1}{2}$ ) ( $\frac{1}{2} - u$ , 0,  $\frac{1}{2}$ ) (u,  $\frac{1}{2}$ ,  $\frac{1}{2}$ ) ( $\bar{u}$ ,  $\frac{1}{2}$ ,  $\frac{1}{2}$ ) (0, u, 0) (0,  $\bar{u}$ , 0) (0,  $\frac{1}{2} + u$ ,  $\frac{1}{2}$ ) (0,  $\frac{1}{2} - u$ ,  $\frac{1}{2}$ ) ( $\frac{1}{2}$ ,  $\frac{1}{2} + u$ , 0) ( $\frac{1}{2}$ ,  $\frac{1}{2} - u$ , 0) ( $\frac{1}{2}$ , u,  $\frac{1}{2}$ ) ( $\frac{1}{2}$ ,  $\bar{u}$ ,  $\frac{1}{2}$ ) (0, 0, u) (0, 0,  $\bar{u}$ ) ( $\frac{1}{2}$ , 0,  $\frac{1}{2} + u$ ) ( $\frac{1}{2}$ , 0,  $\frac{1}{2} - u$ ) (0,  $\frac{1}{2}$ ,  $\frac{1}{2} + u$ ) (0,  $\frac{1}{2}$ ,  $\frac{1}{2} - u$ ) ( $\frac{1}{2}$ ,  $\frac{1}{2}$ , u) ( $\frac{1}{2}$ ,  $\frac{1}{2}$ ,  $\bar{u}$ ).

To distinguish between these two possibilities, use will be made of the expression  $I = f(d/n) (A^2 + B^2)$ . Here  $I$  is the intensity of reflection,  $f(d/n)$  will be assumed simply to have smaller values, for a given wavelength, the smaller is  $d/n$ . In all cases under consideration,  $B = 0$ . The following are the values of  $A$  for the (110) and (111) planes.

Arrangement I.

$$(110) \quad A = 2 \bar{S}n (1 + \cos \pi n) + 4 \bar{K} (1 + \cos \pi n) + 4 \bar{C}l \left( (1 + \cos \pi n + 2 \cos \frac{\pi n}{2} + 2 \cos \frac{3\pi n}{2}) \right).$$

$$(111) \quad A = 4 \bar{S}n + 4 \bar{K} \left( \cos \frac{\pi n}{2} + \cos \frac{3\pi n}{2} \right) + 12 \bar{C}l (1 + \cos \pi n).$$

Arrangement II.

$$(110) \quad A = 2 \bar{S}n (1 + \cos \pi n) + 4 \bar{K} (1 + \cos \pi n) + 4 \bar{C}l (1 + \cos \pi n + 2 \cos 2\pi n u + 2 \cos 2\pi n \left( u + \frac{1}{2} \right)).$$

$$(111) \quad A = 4 \bar{S}n + 4 \bar{K} \left( \cos \frac{\pi n}{2} + \cos \frac{3\pi n}{2} \right) + 24 \bar{C}l \cos 2\pi n u.$$

An inspection of these equations shows that for odd values of  $n$  the value of  $A$  becomes identically zero for the (110) plane but not for (111), and that

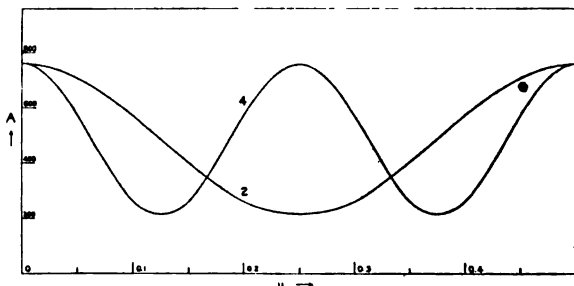


Fig. 1.—Values of  $A$  for  $K_3SnCl_6$  (110).

for even values of  $n$  the value of  $A$  does not become zero. This agrees with the observations.

Since the intensity of the fourth order from (110) was actually greater than that of the second, it is clear, even without any quantitative assumption as to the "normal decline" of intensity, that  $A$  for the fourth order should be greater than  $A$  for the second. By similar reasoning, for (111),  $A$  for the fourth order should be much greater than  $A$  for the third, and

$A$  for the second should probably be greater than  $A$  for the first.<sup>12</sup> Actually, all these conditions are satisfied by the first arrangement. Taking the reflecting powers as proportional to the atomic numbers, for (110),  $A_2:A_4 = 216:760$ , and for (111),  $A_1:A_2:A_3:A_4 = 200:456:200:760$ . In order to determine whether any value of  $u$  can be found which gives suitable values of  $A$  with the second arrangement, the values of  $A$  for the various reflections have been plotted against  $u$ , all possible values of which lie between 0.0 and 0.5. These plots for (110) and (111) are given in Figs. 1 and 2, respectively. It will be seen that for a range of values of  $u$  in the neighborhood of  $1/4$ , all the conditions are satisfied. The numeri-

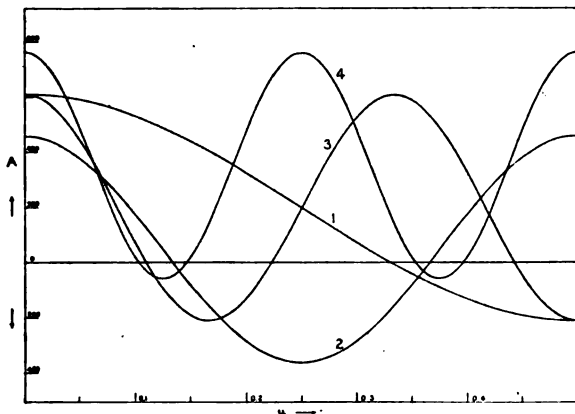


Fig. 2.—Values of  $A$  for  $K_3SnCl_6$  (111).

cal values of  $A$  when  $u = 1/4$  are : for (110),  $A_2:A_4 = 216:760$ , and for (111),  $A_1:A_2:A_3:A_4 = 200:360:200:760$ . It is concluded that either Arrangement I or Arrangement II is possible, and that if II is the correct arrangement, the value of  $u$  lies between 0.2 and 0.3. To discriminate between these two arrangements and to apply further tests to the structure arrived at, use was made of Laue photographs.

#### IV. Laue Photographs of Potassium Chlorostannate.

The source of X-rays for the Laue photographs was a Coolidge tube with a tungsten target, operated at a peak voltage of approximately 54,000. The shortest wave length present, calculated from the well-known relation  $Ve = h\nu$ , was accordingly  $0.23 \text{ \AA}$ . Photographs were made with an X-ray beam passed at small inclinations from the perpendicular to the (111) and (100) faces, the crystals being 5 cm. from the plate. One was made with the beam closely perpendicular to (111).

On these photographs 250 or more spots ordinarily appeared. Gno-

<sup>12</sup> The very small angle of reflection of the first order from (111) makes its intensity less reliable than the others.

monic projections were made graphically<sup>13</sup> from the photographs, and from these projections the indices of each spot were obtained. The distance of each spot on the photograph from the central image, combined with the distance from crystal to plate, determined each angle of reflection. The value of  $n\lambda$  for each spot was then calculated using the expression

$$n\lambda = \frac{2 d_{100} \sin \theta}{\sqrt{h^2 + k^2 + l^2}} \text{ putting } d_{100} \text{ equal to } 9.96 \text{ \AA. as found in Section II.}$$

The smallest value of  $n\lambda$  found for any plane having all odd indices was 0.26, and for any plane having any even index, 0.57. Thus no planes with any even index were found reflecting in the first order. That these facts are accounted for by either of the structures given in the previous section may be seen from an examination of the values of  $A$ . The planes may conveniently be divided into three classes according to the character of the indices.

#### Arrangement I.

*Class 1.* All indices odd.  $n = 1$ ;  $A = 4 \overline{Sn}$ .

*Class 2.* One index even.  $n = 1$ ;  $A = 0$ .  $n = 2$ ;  $A = 4 \overline{Sn} + 8 \overline{K} - 8 \overline{Cl}$ .

*Class 3.* Two indices even.  $n = 1$ ;  $A = 0$ .  $n = 2$ ;  $A = 4 \overline{Sn} - 8 \overline{K} - 8 \overline{Cl}$ .

#### Arrangement II.

*Class 1.* All indices odd.  $n = 1$ ;  $A = 4 \overline{Sn} + 8 \overline{Cl} (\cos 2\pi hu + \cos 2\pi kv + \cos 2\pi lw)$ .

*Class 2.* One index even.  $n = 1$ ;  $A = 0$ .  $n = 2$ ;  $A = 4 \overline{Sn} + 8 \overline{K} + 8 \overline{Cl} (\cos 4\pi hu + \cos 4\pi kv + \cos 4\pi lw)$ .

*Class 3.* Two indices even.  $n = 1$ ;  $A = 0$ .  $n = 2$ ;  $A = 4 \overline{Sn} - 8 \overline{K} + 8 \overline{Cl} (\cos 4\pi hu + \cos 4\pi kv + \cos 4\pi lw)$ .

The relative intensities of spots due to planes of Class I will now be considered. Numerous instances were found in which a plane reflected in the first order somewhat more strongly than another plane having a larger spacing. For instance, a plane of the form  $\{911\}$ , with spacing 1.09 Å., was found to reflect more strongly than one of the form  $\{731\}$ , with spacing 1.30 Å., both, of course, at the same wavelength, and a plane of the form  $\{953\}$ , with spacing 0.929 Å., reflected at least twice as strongly as one of the form  $\{773\}$ , with spacing 0.963 Å. In some cases where two forms which it was desired to compare gave no planes reflecting the same wavelength, the method of plotting estimated intensities against wavelength was employed; it was necessary to exercise care in making comparisons in the neighborhood of the critical absorptions of tin ( $\lambda = 0.424$  Å.) and of silver ( $\lambda = 0.485$  Å.). In this way the instances given in Table II were noted where one plane clearly reflected more strongly than another having the same or a larger spacing.

If Arrangement I were correct, it would be expected that the intensity of reflection would always be less the smaller the spacing of the plane. Since the observations are not in accord with this, it remains to be deter-

<sup>13</sup> Wyckoff, *Am. J. Sci.*, 50, 322 (1920).

TABLE II  
ABNORMAL INTENSITY RELATIONS FOR POTASSIUM CHLOROSTANNATE

Forms giving		Corresponding spacings of planes		Corresponding values of $A$ calculated for $u = 0.245$	
(1) greater observed intensity	(2) smaller observed intensity	(1)	(2)	(1)	(2)
{911}	{731}	1.093	1.298	247	162
{953}	{773}	0.866	0.922	247	128
{951}	{755}	0.931	1.006	264	213
{553}	{731}	1.688	1.688	230	162
{551}	{711}	1.952	1.952	247	179
{931}	{753}	1.093	1.200	230	179
{911}	{751}	1.200	1.327	247	196
{973}	{11.3.3}	0.717	0.772	196	128
{995}	{11.5.3}	0.532	0.642	298	162
{13.5.1}	{11.5.3}	0.511	0.642	281	162
{13.5.1}	{11.7.3}	0.511	0.556	281	110
{13.3.1}	{11.7.3}	0.556	0.556	247	110
{973}	{11.3.1}	0.717	0.760	196	145

mined whether a value of  $u$  can be found in the second arrangement which accounts systematically for the observed abnormalities.

The values for  $A$  for a number of planes given in Table II are shown in Fig. 3 plotted against  $u$ . An examination of these plots shows that the

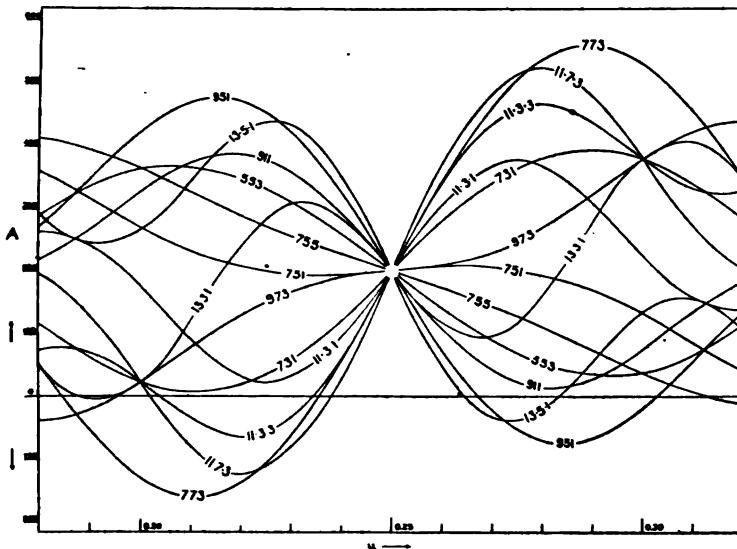


Fig. 3.—Values of  $A$  for first order reflections of various planes of Class 1 of  $K_2SnCl_6$  or  $(NH_4)_2SnCl_6$ .

value of  $u$  cannot be just 0.25, but must lie below 0.25. Indeed all of the inequalities given in Table II are satisfied if  $u$  is given some value immediately below 0.25, and it was not found possible to establish any



inequalities that were not thus satisfied. The conclusion that  $\mu$  lies only a little below 0.25 receives some support from the fact that no very great abnormalities were found in the intensities.

Since first-order reflections are entirely absent in Classes 2 and 3, spots due to planes in these classes have been interpreted as pure second-order reflections for values of  $n\lambda$  below 0.96. When the planes of Class 2 were examined among themselves it was not found possible to establish with certainty inequalities in the manner done for Class 1. This fact is explicable if  $\mu$  is only a little below 0.25; for not only is the value of  $A$  the same for each plane of Class 2 when  $\mu = 0.25$ , but also  $dA/d\mu$  is zero at this point. The same is true for Class 3.

It is of interest that under comparable conditions planes of Class 2 reflected with about the same intensity as those of Class 3. In the immediate neighborhood of  $\mu = 1/4$ , all planes of Class 2 have  $A = 4\overline{Sn} + 8\overline{K} - 8\overline{Cl}$ , and those of Class 3,  $A = 4\overline{Sn} - 8\overline{K} + 8\overline{Cl}$ . These two expressions become equal if  $\overline{K} = \overline{Cl}$  as has been found to be at least approximately the case in potassium chloride.<sup>14</sup> If Arrangement I were correct, Class 2 might be expected to reflect more strongly than Class 1.

The various tests afforded by the data, which involve no quantitative assumption concerning "normal decline" of intensity, and only rough assumptions as to the relative reflecting powers of the atoms, lead then to the conclusion that the coördinates of the atoms are given by Arrangement II, the value of  $\mu$  being probably not far from 0.245.

### V. Spectral Photographs of Ammonium Chlorostannate.

No previous crystallographic work on ammonium chlorostannate was found in the literature. The crystals were prepared in the same manner as those of the potassium compound. The form chiefly developed was the octahedron with a frequent occurrence of cube faces. Two density determinations each gave the value 2.39 g. per cc., in good agreement with 2.387 given by Schröder.<sup>15</sup> Small crystals appeared optically isotropic when examined between crossed nicols in the polarizing microscope. A very good octahedral cleavage was observed.

Spectra from the (100) and (111) planes were photographed. In the latter case potassium chlorostannate was used as the reference crystal. The only noticeable difference in the relative intensities of the (111) spectra of the two substances was a weakening of the second order in the ammonium salt. The results of these measurements are given in Table III.

In applying the theory of space groups to ammonium chlorostannate account must be taken of the hydrogen atoms. If these be assumed to be all equivalent, then 32 positions are required for them in addition to

<sup>14</sup> W. H. and W. L. Bragg, "X-rays and Crystal Structure," G. Bell and Sons Ltd., London, 1916, p. 188.

<sup>15</sup> Schröder, *Jahresber.*, 1874, 177.

TABLE III  
REFLECTION DATA FOR AMMONIUM CHLOROSTANNATE

Plane	Line	Observed angle of reflection	$n$	$d_{100}$	Intensity
(100)	$\beta$	$3^{\circ} 7'$	2	(10.03)	
	$\alpha_1$	3 32		(9.98)	Medium
	$\beta$	6 15	4	10.02	
	$\alpha_1$	7 2		10.00	Strong
	$\beta$	9 23	6	10.03	
	$\alpha_1$	10 33		10.03	Weak
	$\beta$	12 32	8	10.05	
	$\alpha_1$	14 8		10.03	Medium weak
(111)	$\beta$	2 41	1	(10.09)	
	$\alpha_1$	3 1		(10.07)	Strong
	$\beta$	5 23	2	10.07	
	$\alpha_1$	6 4		10.03	Medium strong
	$\beta$	8 4	3	10.09	
	$\alpha_1$	9 7		10.04	Weak
	$\beta$	10 48	4	10.08	
	$\alpha_1$	12 10		10.06	Medium

Mean 10.05Å.

Calc. from density 10.05

the 8, 4, and 24 positions as in the case of potassium salt. The space-groups  $O^3$  and  $O_h^6$  satisfy the conditions, and both lead to the same arrangement, namely, the tin, and chlorine atoms are located as in the potassium salt, the nitrogen takes the place of the potassium, and the hydrogen atoms are arranged on cube diagonals, the determination of one parameter being required to fix their position. This parameter could be given such a value that the hydrogen atoms would be grouped close to the nitrogen so as to form a tetrahedron, as they have been supposed to do in ammonium chloride.<sup>16</sup> In the following treatment the reflecting power of the hydrogen atoms has been assumed to be negligible. The expressions for  $A$  then become like those of the previous case except that  $\bar{N}$  replaces  $\bar{K}$ .

From the relative intensities of the spectra given in Table III, it is clear that for (100),  $A$  for the fourth order must be greater than  $A$  for the second, and  $A$  for the eighth order must be greater than  $A$  for the sixth. And for (111),  $A$  for the fourth order must be greater than  $A$  for the third. These conditions are all satisfied if  $u$  has a value near  $1/4$ . At  $u = 1/4$ , the relative values of  $A$  for the (100) spectra, come out 280:664:280:664, and for the (111) spectra 200:264:200:664.

## VI. Laue Photographs of Ammonium Chlorostannate.

Crystal plates were ground a few degrees from parallel to the planes (111) and (100). The Laue photographs obtained with them were treated

<sup>16</sup> Langmuir, THIS JOURNAL, 41, 1547 (1919).

in the same way as the previous ones. Only planes having all odd indices were found reflecting in the first order.

For the planes of Class 1 it was found possible to establish a series of inequalities in the same manner as for potassium chlorostannate. The instances noted are given in Table IV.

TABLE IV  
ABNORMAL INTENSITY RELATIONS FOR AMMONIUM CHLOROSTANNATE

Forms giving		Corresponding spacings of planes		Corresponding values of $A$ calculated for $\mu = 0.245$	
(1) greater observed intensity	(2) smaller observed intensity	(1)	(2)	(1)	(2)
{951}	{773}	0.972	0.972	264	128
{951}	{755}	0.972	1.010	264	213
{553}	{731}	1.310	1.310	230	162
{975}	{773}	0.808	0.972	230	128
{975}	{973}	0.808	0.852	230	196
{973}	{11.3.3}	0.852	0.852	196	128
{975}	{11.5.1}	0.808	0.829	230	179
{13.5.1}	{11.5.1}	0.720	0.829	281	179
{13.5.1}	{11.3.3}	0.720	0.852	281	128
{13.3.3}	{11.3.3}	0.735	0.852	230	128
{911}	{751}	1.103	1.161	247	196
{911}	{753}	1.103	1.103	247	179
{13.5.1}	{11.7.5}	0.720	0.720	281	145
{13.5.1}	{11.5.5}	0.720	0.768	281	196
{995}	{11.5.5}	0.735	0.768	298	196
{953}	{771}	0.938	1.010	247	145
{951}	{771}	0.972	1.010	264	145
{13.5.1}	{11.5.3}	0.720	0.807	281	162
{975}	{11.5.3}	0.807	0.807	230	162

Since no attempt was made to have the crystals of the two substances oriented in the same way when the photographs were taken, the pairs of planes which happened to permit comparisons were not always the same. But just as with the potassium salt, all of the inequalities which were established were satisfied by values of  $\mu$  slightly less than 0.25.

When planes of one of the classes 2 or 3 were examined among themselves, it was not found possible to establish inequalities in the values of  $A$ . From the same arguments as in the previous case the value of  $\mu$  is concluded to be not far from 0.245.

When spots due to planes of Class 2 were compared with those from Class 3, it was found that, unlike the result with the potassium salt, those of Class 3 were distinctly more intense than those of Class 2. For instance, on two different photographs planes of the form {621},  $d/n = 0.778$ , reflected more strongly than those of form {521},  $d/n = 0.910$ , in spite of the smaller value of  $d/n$ ; similarly {601}  $d/n = 0.819$ , reflected more strongly than {501},  $d/n = 0.977$ . To explain this with the above struc-

ture it is necessary to assume no more than that the reflecting powers  $\overline{Sn}$ ,  $\overline{Cl}$ , and  $\overline{N}$  differ appreciably in the order named, that of tin being greatest. For the expressions for  $A$  are substantially: *Class 2*,  $A = 4\overline{Sn} - 8(\overline{Cl} - \overline{N})$ ; *Class 3*,  $A = 4\overline{Sn} + 8(\overline{Cl} - \overline{N})$ .

If this interpretation of these intensities is correct, the value of  $A$  for planes of Class 2 is appreciably less than  $4\overline{Sn}$ , and for planes of Class 3 appreciably greater than  $4\overline{Sn}$ . Now the planes of Class 1 may be subdivided into: (1a) those for which the calculated value of  $A$  is  $4\overline{Sn}$  plus a positive increment due to chlorine atoms alone, and (1b) those for which it is  $4\overline{Sn}$  plus a negative increment due to the chlorine atoms. Certainly then planes of Class 1a should reflect a given wavelength more strongly than planes of Class 2 having the same value of  $d/n$ , and those of Class 1b should reflect less strongly than those of Class 3. A number of intensity comparisons were found possible which confirmed these conclusions. For instance, a plane of the form  $\{951\}$ ,  $d/n = 0.972$ , reflected at  $n\lambda = 0.45$  more strongly than one of the form  $\{431\}$ ,  $d/n = 0.986$ , reflected at  $n\lambda = 0.90$ , and a plane of the form  $\{421\}$ ,  $d/n = 1.197$ , reflected around  $n\lambda = 0.60$  more strongly than one of the form  $\{731\}$ ,  $d/n = 1.703$ , at  $n\lambda = 0.30$  in spite of the more favorable value of  $d/n$  in the latter form. No inequalities in the reverse sense were found.

The X-ray data for ammonium chlorostannate thus lead to the same type of structure that was deduced for the potassium salt and, as far as can be determined, to about the same value of  $u$ .

## VII. Discussion of the Crystal Structures.

The structure deduced for potassium chlorostannate involves the following relations. Each potassium atom has 4 tin atoms equally distant from it. Each tin atom has 8 potassium atoms equally distant from it. Each chlorine atom has 4 potassium atoms equally distant, and each po-

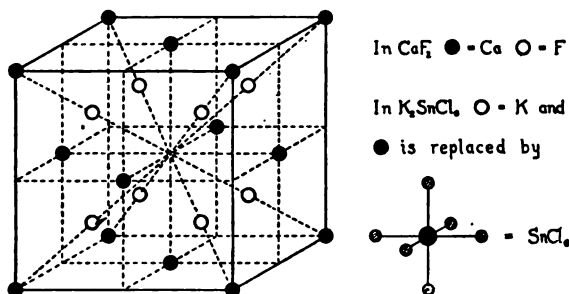


Fig. 4.—Arrangement of the atoms in  $CaF_2$  and in  $K_2SnCl_6$ .

tassium atom has 12 chlorine atoms equally distant, but each chlorine atom is at a shorter distance from one tin atom than from any other, and each tin atom has 6 chlorine atoms at this distance from it. The structure

may thus be regarded as an assemblage of potassium atoms and  $\text{SnCl}_6$  groups.

If the potassium atoms and  $\text{SnCl}_6$  groups be considered electrically charged so that the crystal is built up of  $\text{K}^+$  and  $\text{SnCl}_6^-$  ions, the structure is then ionically similar to that of calcium fluoride,<sup>17</sup>  $\text{K}^+$  replacing  $\text{F}^-$ , and  $\text{SnCl}_6^-$  replacing  $\text{Ca}^{++}$ .

These relations are illustrated by Fig. 4.

The cohesive relations of a polar substance may well be presumed to depend to a considerable extent upon the electrostatic attractions and repulsions of the constituent ions; and since the arrangement of the ions is the same in the chlorostannates as in calcium fluoride, it is not surprising that, in spite of the dissimilarity in atomic constitution, these substances show the same cleavage, namely, along the octahedral planes.<sup>18</sup>

The shortest distances between the various unlike atoms are given in Table V. These distances are accurate to within a few tenths of 1%, except the distance from the tin to the chlorine atoms, whose calculation involves the value of  $\mu$ . It is possible that this distance is several per cent. too high, but it can hardly be much too low.

TABLE V  
DISTANCES BETWEEN THE ATOMS IN  $10^{-8}$  CM.

Substance	$d_{100}$	Sn and Cl	K or N and Sn	K or N and Cl
$\text{K}_2\text{SnCl}_6$	9.96	2.44	4.31	3.52
$(\text{NH}_4)_2\text{SnCl}_6$	10.05	2.46	4.35	3.55

### VIII. Summary.

With the aid of spectral photographs and unsymmetrical Laue photographs, the crystal structures of potassium chlorostannate and ammonium chlorostannate have been determined; and these structures have been shown to be closely similar to each other. It was found possible to carry out the analyses without making any quantitative assumption concerning "normal decline" of intensity, and with only rough assumptions as to the relative reflecting powers of the atoms. The results lead to the conclusion that 6 equivalent chlorine atoms are grouped about each tin atom; and the structure is accordingly regarded as built up of  $\text{SnCl}_6^-$  ions and  $\text{K}^+$  or  $\text{NH}_4^+$  ions, in the way shown in Fig. 4. The similarity of these substances, in structure and cleavage, to calcium fluoride is pointed out, as being in accordance with this conclusion.

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<sup>17</sup> W. L. Bragg, *Proc. Roy. Soc.*, **89A**, 474 (1914).

<sup>18</sup> Ref. 2, p. 206.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF MICHIGAN.]

## THE RELATION OF ANOMALOUS OSMOSE TO THE SWELLING OF COLLOIDAL MATERIAL.

BY F. E. BARTELL AND L. B. SIMS.

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### Introduction.

During the progress of the work on anomalous osmose in this laboratory, the writers have been greatly impressed by the similarity noted between the phenomena of the swelling of gels, the swelling of organic tissues, the diffusion of liquids through living tissues, and the anomalous osmose observed with different types of membranes when used with solutions of electrolytes. After a rather extensive investigation of these related processes it seems obvious that a satisfactory understanding of the principles underlying them can be obtained only by the study of the principles underlying the phenomena of anomalous osmose.

Much work has been done on the swelling of various materials and many theories have from time to time been presented to account for this phenomenon. Among the more important of these theories are: (a) the capillary theory, (b) the osmotic theory, (c) the lipid membrane theory, (d) the colloid chemical theory, (e) the repulsion theory, (f) the diffusion theory, and (g) the solid solution theory.

(a) The capillary theory assumes that swelling takes place by passage of liquid through small pores, the impelling force being the difference in surface tension between solvent and solution. This theory does not explain the cases in which the flow of solution is in the direction opposite to the one that would be predicted from difference in surface tensions.

(b) According to the osmotic theory<sup>1,2</sup> liquids pass into the material and cause swelling because of the difference of osmotic pressure between the external and internal solutions. This theory does not *explain* abnormal effects in acid and alkaline solutions, nor cases where the flow is from concentrated to dilute solution.

(c) Overton's<sup>3</sup> lipid membrane theory is based on the assumption that liquids pass into cells by dissolving in a membrane which surrounds them. Though some substances undoubtedly pass in by dissolving in the membrane, this theory does not explain the passage of a large number of substances which are not soluble in the membrane; nor does it explain how

<sup>1</sup> Pfeffer and de Vries, "Pflanzen Physiol.," Leipzig, 1, 116 (1897).

<sup>2</sup> An article on osmosis and swelling of gelatin by C. P. Smith appeared in THIS JOURNAL, 43, 1350 (1921) just as the present article was about to be sent to the editor. Many of the results given in the article by Smith can be accounted for by applying the principles of anomalous osmose and are in accord with some of the results obtained by the present authors in their work.

<sup>3</sup> Overton, Z. physik. chem., 22, 189 (1897).

the soluble substances are able to pass out again on the other side of the membrane, as they must be considered to do.

(d) In the colloid chemical theory<sup>4</sup> we are to consider that the colloid cell is the unit, and that there is no surrounding membrane. Cells swell in acid and alkali because acid and alkali increase their hydration power. In other words, colloids swell in acid and alkali because acid and alkali cause them to swell, which is offering no explanation of the basic reason nor the mechanics of the process.

(e) The repulsion theory<sup>5</sup> explains swelling on the assumption that all the colloid particles become charged with electricity of the same sign. This causes an electrostatic repulsion and the colloid increases in size. It may be pointed out that gelatin at its iso-electric point has been found to swell more than 600%<sup>6</sup> and while the swelling does increase with increase of concentration of acid or alkali, which would increase the charge, it increases only up to a certain concentration. Above a certain concentration with either acid or alkali a decrease in swelling is observed, even though the charge on the particles may increase. The electrostatic charge undoubtedly has an important effect, but this one factor alone does not seem quite comprehensive enough to cover the whole case.

(f) Proctor and Wilson<sup>7</sup> assume that such substances as gelatin behave amphotERICALLY and, in acid and alkali, form highly ionized salts, the non-colloid ion of which, in diffusing out, exerts a pull that swells the gel. If this is to be accepted as a general explanation of the swelling of animal and vegetable material, it must be considered that there are amphoteric substances in all animal and vegetable material which are capable of forming ionizable salts that cause swelling by diffusion. On this basis such material should swell in any concentration of acid or alkali, yet an actual shrinking has been noted in some cases.

(g) The solid solution theory was formulated by J. R. Katz<sup>8</sup> who believes that amorphous swelling substances differ from liquids only in viscosity, that swelling may be regarded as the mixing of a highly viscous liquid with some miscible liquid to form a solid solution. This theory offers no explanation of the swelling of a substance in a liquid of one concentration, while an actual shrinking is observed with the substance in this liquid at a slightly different concentration.

It must be admitted that the problem in question is complex. No single, simple theory can account for all the facts. Undoubtedly nearly all the fundamental concepts of the above theories must be used in order

<sup>4</sup> Fischer, "Oedema and Nephritis," John Wiley and Sons, 1915, p. 162.

<sup>5</sup> Tolman, *THIS JOURNAL*, 40, 246 (1918).

<sup>6</sup> Lloyd, *Biochem. J.*, 14, 147 (1920).

<sup>7</sup> Proctor and Wilson, *J. Chem. Soc.*, 109, 307 (1916).

<sup>8</sup> Katz, *Z. physiol. Chem.*, 96, 255 (1916); *Verslag Akad. Wetenschappen, Amsterdam*, 1911, 958-75; *C. A.*, 5, 3533 (1911).

to make a satisfactory "explanation," or to work out a comprehensive theory which will cover all cases. We must incorporate in addition to the above concepts, others which will take care of those cases in which the above fail to apply. The incorporation of the principles underlying anomalous osmose will go far toward taking care of many of the heretofore unexplained facts.

In much of recent work on anomalous osmose in this laboratory there have been observed so many factors that seem to have an effect on the phenomenon of swelling as well as on the phenomenon of anomalous osmose that the authors have sought to make a comparative study of these processes and to correlate them.

### Results of Some Experiments on Osmosis.

The most striking anomalous effects have been obtained when a fairly permeable membrane such as collodion has been used with solutions of electrolytes. When osmotic effects are plotted against concentration of solution, or better, logarithm of concentration, a striking N-shaped curve is obtained;<sup>9</sup> for instance, as the concentration of the solution is increased the osmotic effect first increases, then falls off, then increases again. These effects are readily shown in the following tables and curves.

TABLE I

OSMOSE OF ACIDS OF VARIOUS CONCENTRATIONS WITH CALF'S BLADDER AND GOLDBEATER'S SKIN<sup>a</sup>  
(In mm.)

Conc. of Acid, <i>M</i>	0.000,001	0.00001	0.0001	0.001	0.01	0.1	1	10
HCl								
Calf's bladder.....	0	+2	+2.5	+3	+12	-4	-63	+47
HNO <sub>3</sub>								
Gold beater's skin (A)...	...	...	+1	+2.5	+14.5	-2	-28.5 <sup>b</sup>	+55
HCl								
Gold beater's skin (B)...	-4	-5	-4	-2	0	-15	-43	+13

<sup>a</sup> The data for gold beater's skin A except the values for 10 *M* acid and alkali were obtained from work by Bartell and Madison.<sup>10</sup> The values for 10 *M* acid and alkali were obtained at a later date.

<sup>b</sup> 0.05 *M* conc. HNO<sub>3</sub>.

TABLE II

OSMOSE OF VARIOUS CONCENTRATIONS OF SODIUM HYDROXIDE WITH GOLDBEATER'S SKIN<sup>a</sup>

Conc. of NaOH, <i>M</i>	0.000,001	0.00001	0.0001	0.001	0.01	0.1	0.5	10
Goldbeater's skin (A)...	...	...	+1.5	+3	+5	+1	-5.5	+40
Goldbeater's skin (B)...	...	-3	-5	-18	+5	-0.5	-46	+35

<sup>a</sup> Jacques Loeb has also obtained similar N-shaped curves for collodion membranes, *J. Gen. Physiol.*, 2, Nos. 4 and 5 (1920).

<sup>10</sup> Bartell and Madison, *J. Phys. Chem.*, 24, 444, 593 (1920).



Goldbeater's skin A and B were different grades, and Skin A was used with double cells, while the Skin B was used with single cells (*i. e.*, single compartment cells which were placed in a much larger volume of water than was present in the 2-compartment cell), and started under a hydrostatic head of 100 mm.

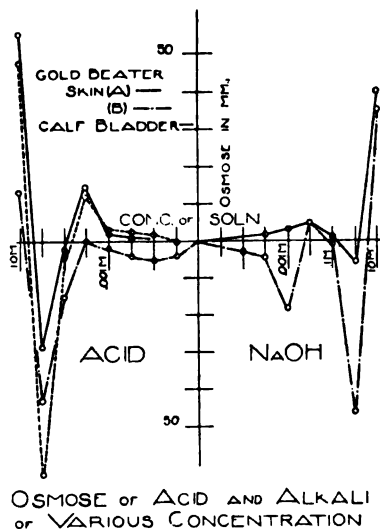


Fig. 1.

(In all figures log. of conc. is plotted on the horizontal.)

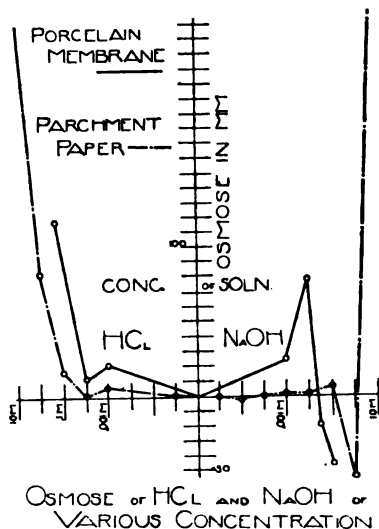


Fig. 2.—Osmose of hydrochloric acid and sodium hydroxide of various concentrations with parchment paper and porcelain membranes.

The experiments with calf's bladder were carried out in single cells but were started under no hydrostatic pressure.

TABLE III

OSMOSE OF HYDROCHLORIC ACID OF VARIOUS CONCENTRATIONS WITH PARCHMENT PAPER AND PORCELAIN MEMBRANES<sup>a</sup>

Conc. of HCl, M	0.000,001	0.00001	0.0001	0.001	0.01	0.05	0.1	0.2	1	10
Porcelain.....	...	...	...	+23	+12	+69.5	+64	+118	...	...
Parchment.....	+0.5	0	+7	0	+2	...	+16	...	+84	+495

TABLE IV

OSMOSE OF SODIUM HYDROXIDE OF VARIOUS CONCENTRATIONS WITH PARCHMENT PAPER AND PORCELAIN MEMBRANES<sup>a</sup>

Conc. of NaOH, M	0.000,001	0.00001	0.0001	0.001	0.01	0.05	0.1	0.2	1	10
Porcelain.....	...	...	...	+25	+75	-14.5	-45	...	...	...
Parchment.....	0	-1	0	+1	+1	...	+6	...	-55	+360

<sup>a</sup> The data for porcelain membrane were obtained from previous work by Bartell and Hocker.<sup>11</sup> The experiments with parchment paper as a membrane were carried out in single cells and were started with no hydrostatic head.

It will be noted that the peculiar N-shaped curves were obtained in every case and that they are very similar even though the nature of the membranes was widely different. From the results obtained, the con-

<sup>11</sup> Bartell and Hocker, *THIS JOURNAL*, 38, 1029, 1036 (1916).

clusion was reached that forces other than those responsible for the normal osmotic tendency were operative within the system.

In previous papers<sup>10</sup> from this laboratory the electrical effects due to electrical orientation of the cell membrane system have been discussed; therefore, in this paper only a few general statements relative to the theory will be given.

According to Helmholtz, when almost any substance is placed in a solution, a double electrical layer (Helmholtz layer) is set up, the substance carrying one sign, and the liquid bathing it the other. If the solution is of an electrolyte, it is generally assumed that the signs of the charges are dependent upon the selective adsorption of the ions by the substance. For example, an acid gives a positive charge due to hydrogen-ion adsorption, and a base gives a negative charge due to hydroxyl-ion adsorption.

We assume, then, that two determining factors must always be considered, namely, the effect due to the electric charge of the capillary pore wall with respect to the charge of the liquid bathing it (which we have called the capillary system), and to the orientation of the electrical potentials existing between the two faces of the membrane (membrane system). The magnitudes of these two electrical factors are dependent upon the extent of diffusion of electrolyte through the membrane, upon the relative migration velocities of the ions, and upon the extent of selective ion adsorption.

The osmose due to this superimposed effect is assumed to be caused by the passage of a charged liquid layer along the walls of the capillary pores of the membrane under a driving force of potential which acts as though it were set up between the two faces of the membrane.

### **Relation of Swelling of Gel to Osmotic Effects.**

In relating the process of swelling of gel to the process of osmose we may assume that a gel is built up of a framework of cells, that some unit of this framework may be considered to function as a fairly permeable membrane which would make it possible for this unit of the system to respond to the influences responsible for the process of anomalous osmose; in fact we assume that osmotic flow of solution would actually take place through this portion of the system.

Suppose we consider a cell or group of cells so arranged that within this unit liquid will be enclosed by the membrane thus formed, while at the same time liquid, either of the same or of different concentration, will bathe this membrane on the outside. If we assume the existence of such a membrane we need only to have in mind a picture of an osmotic system and its related electrical factors in order to predict the behavior of the cell system. It seems reasonable to assume that all the factors responsible for anomalous osmose would likewise be in evidence in the process of swelling of cellular gels.

### Theory Applied to Swelling of Colloid Material.

In a previous paper we have shown that four distinctly different types of electrification of a membrane system may exist.<sup>10</sup> These four cases may be applied directly to the cell system within gel or other colloid material, as shown in Fig. 3, each diagram of which represents a single osmotic unit of the gel.

An electrical orientation of the cell system as indicated in A would result in operation of the superimposed effect, due to electrical forces,

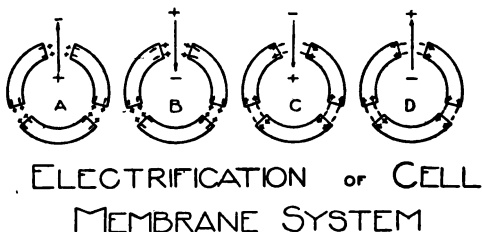


Fig. 3.

tending to cause a flow of solution from the cell; this would produce a shrinking of the cell walls.

Systems represented by Cases B and C would both tend to give swelling effects (comparable to negative osmose) while the system represented by D would tend to give an abnormally positive osmotic effect which would result in a shrinking of the cell.

If it be true that a relationship of this type between osmose and swelling does exist, it should be noted that swelling effects of materials containing pure water, placed in an aqueous solution, should correspond to a negative osmotic tendency, while shrinking effects should correspond to an abnormally positive osmotic tendency.

It must be remembered, however, that this electrical force may be only one of several forces acting. Experiments carried out in this laboratory, but not as yet published, seem to indicate that negative and positive adsorption may have a marked effect on both osmose and swelling.

As a working hypothesis the authors assume that a gel may be considered to be composed essentially of a framework of membranes and that the theory accounting for the flow of liquid through membranes likewise accounts to a certain extent for the flow of solution into a cellular gel. We hold the view that swelling is the result of imbibition (a process which is not well understood and which may be due either to a capillary action or to intermolecular reactions) together with the operation of effects which produce anomalous osmose. From this it would follow, in swelling, that (1) the tendency for normal osmose is always operative; (2) solution in the membrane may take place in some instances; (3) forces of attraction and

repulsion are operative; (4) capillarity plays a part; (5) negative or positive adsorption of solute may have its effect; (6) electrical effects due to electrical orientation of the system may enter in; (7) swelling unaccompanied by electrical effects may occur, as with solutions of non-electrolytes with some gels.

In order to compare as closely as possible anomalous osmotic effects with swelling effects different series of experiments were carried out.

### Swelling of Laminaria.

The first series of experiments was made in order to obtain one example of each of the four cases above mentioned. Parchment paper membranes were used for the osmotic experiments while laminaria which had stood for about 24 hours in distilled water was used for the swelling experiments. Laminaria and parchment paper were chosen because both are vegetable materials.

TABLE V

FOUR CASES OF SWELLING WITH LAMINARIA, TOGETHER WITH OSMOSE VALUES OBTAINED WITH THE SAME SOLUTIONS

Case	Solution	Conc.	Initial Wt.	Final Wt.	Swelling	Osmose
		M	G.	G.	%	Mm.
A	K citrate	0.05	1.243	1.232	- 0.89	+38
B	NaOH	0.0001	0.540	1.081	+100.00	-4
C	HCl	0.0001	0.682	1.103	+ 62.00	-3
D	AlCl <sub>3</sub>	0.05	1.750	1.646	- 5.95	+59

The four solutions used were selected because, when tested in osmotic systems, each was found to give a different one of the four possible cases of electrical orientation (Fig. 3). From the results in this table it is noted that the swelling effects fit in nicely with the anomalous osmotic effects. Those solutions which showed negative osmotic tendency with parchment, produced a swelling effect with laminaria, and those which showed a positive osmotic tendency produced a shrinking of the laminaria.

In the second series, osmotic experiments with parchment paper and swelling experiments with laminaria were carried out using solutions of different concentrations. The results are given in the following tables and curves.

TABLE VI

OSMOSE OF HYDROCHLORIC ACID AND SODIUM HYDROXIDE IN DOUBLE CELLS WITH PARCHMENT PAPER MEMBRANE. TIME OF OSMOSE, 8 HOURS. OSMOTIC EFFECTS ARE EXPRESSED IN TERMS OF RISE IN MILLIMETERS

Conc. of Soln., M	0.000,001	0.00001	0.0001	0.001	0.01	0.1	1	10
HCl.....	0	-5	-3	-1.5	0	+18.5	+33	+675
NaOH.....	.	...	-4	0	+2	-8	-25	+354

TABLE VII  
SWELLING OF LAMINARIA\*

A stick of laminaria was allowed to swell for about 24 hours, then was cut into thin sections. Each section was weighed, placed in acid or alkali for 1 hour, and weighed again.

Soln.	Conc.	Wt. after 1 hr. in		Swelling
		Initial wt.	Acid or alk.	
	<i>M</i>	G.	G.	%
HCl	10.0	0.906	0.590	- 34.8
	1.0	0.590	0.518	- 12.2
	0.1	0.864	0.781	- 9.62
	0.01	0.690	0.753	+ 9.13
	0.001	0.790	1.030	+ 30.4
	0.0001	0.682	1.103	+ 61.7
	0.00001	0.611	1.060	+ 73.4
	0.000,001	0.690	1.108	+ 60.6
H <sub>2</sub> O.....		0.765	1.086	+ 41.9
NaOH	0.00001	0.717	1.157	+ 61.4
	0.0001	0.540	1.081	+100.2
	0.001	0.582	1.121	+ 92.7
	0.01	0.704	1.160	+ 64.8
	0.1	0.685	1.090	+ 59.2
	1.	0.571	0.823	+ 44.2
	10.	0.590	0.590	0

\* A minus sign (-) indicates shrinking of the gel.

TABLE VIII  
SWELLING OF LAMINARIA

Swelling in acid and alkali when previously allowed to swell almost to a maximum in water for approximately 48 hours

Soln.	Conc. <i>M</i>	Initial wt. G.	Wt. after 22 hrs. in soln.		Swelling %
			G.		
HCl	10	1.136	1.070	- 5.8	
	1	1.228	1.111	- 9.4	
	0.1	1.531	1.332	-13.0	
	0.01	1.213	1.165	- 3.96	
	0.001	1.901	1.939	+ 1.99	
	0.0001	1.181	1.193	+ 1.02	
	0.00001	1.496	1.533	+ 2.47	
	0.000001	1.586	1.618	+ 2.20	
H <sub>2</sub> O	.....	1.463	1.493	+ 2.05	
NaOH	0.000001	1.243	1.261	+ 1.45	
	0.00001	0.948	0.956	+ 0.84	
	0.0001	1.269	1.301	+ 2.52	
	0.001	0.933	0.968	+ 3.75	
	0.01	1.323	1.403	+ 6.05	
	0.1	1.463	1.684	+15.1	
	1.	1.481	1.583	+ 6.89	
	10.	1.966	1.668	-15.2	

TABLE IX  
OSMOSE OF CHLORIDES

In double cells with parchment paper membrane, acid and alkali throughout the cell

Molar conc. of acid or alkali throughout	Time of osmose, 6 hours		
	Osmose Set A 0.05 M KCl	Osmose Set B 0.05 M MgCl <sub>2</sub>	Osmose Set C 0.05 M AlCl <sub>3</sub>
	Mm.	Mm.	Mm.
0.001 HCl	3	6.5	18
0.0001 HCl	6	9.5	24
Dist. H <sub>2</sub> O	6	7	25
0.0001 NaOH	4.5	6	21
0.001 NaOH	3	5	20.5

TABLE X  
SWELLING OF LAMINARIA

First soaked in acid or alkali, then allowed to swell in a solution of chloride in acid or alkali of the same concentration as the acid or alkali in which it was soaked. Time of swelling, 5 hours

Molar conc. of acid or alkali used	Set A 0.05 M KCl	Set B 0.05 M MgCl <sub>2</sub>	Set C 0.05 M AlCl <sub>3</sub>
	%	%	%
0.001 HCl	-1.69	-1.49	-2.33
0.0001 HCl	-3.2	-6.96	-7.87
Dist. H <sub>2</sub> O	-2.23	-7.07	-9.08
0.0001 NaOH	-2.64	-5.68	-7.46
0.001 NaOH	-0.735	-5.12	-6.90

Figure 4 gives the curves obtained from Tables VI and VII. The osmose of hydrochloric acid and sodium hydroxide in double cells with parchment

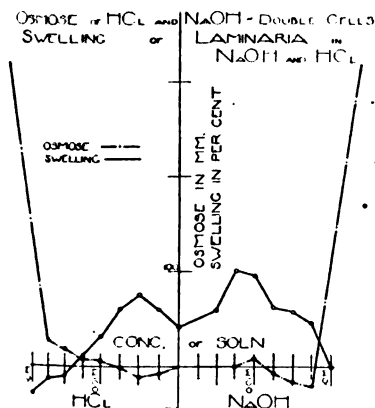


Fig. 4.

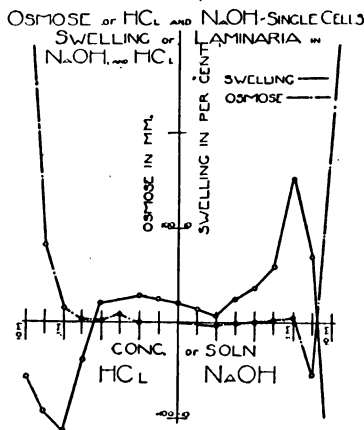


Fig. 5.

paper membrane is plotted on the same coördinates as the swelling of laminaria in hydrochloric acid and sodium hydroxide. The laminaria was softened in distilled water until it could be cut, was then cut into thin slices, each slice weighed, and placed in a solution of acid or alkali for one hour, and weighed again.

Figure 5 gives the curves obtained from Table VIII and from the values of osmose with parchment from Tables III and IV. The osmose of hydrochloric acid and sodium hydroxide in single cells with parchment paper membrane is plotted on the same coördinates as the swelling of laminaria in hydrochloric acid and sodium hydroxide. In this case the laminaria was cut in thin sections and then placed in distilled water until it had swollen nearly to a maximum in the water, when it was placed in solutions of acid and alkali and allowed to swell further. This gave a curve similar to that for laminaria in Fig. 4 but the swelling was, for the most part, not so great and the maximum points came at higher concentrations.

Figure 6 gives the curves obtained from Tables IX and X. The osmose of chlorides in double cells using parchment paper membrane with the same

RELATION OF OSMOSE TO SWELLING WITH  
SALT SOLUTIONS

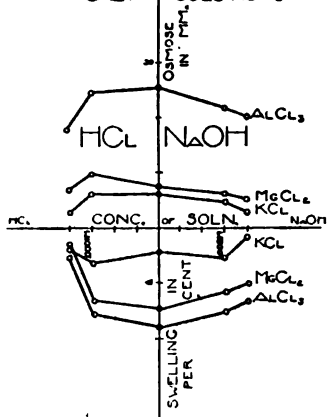


Fig. 6.

concentration of acid or alkali in both compartments of the cell is plotted on the same coördinates as the swelling of laminaria in solutions of chlorides in acid and alkali. The laminaria had previously been soaked in acid and alkali of the same concentration as that in the chloride solution in which it was subsequently allowed to swell.

The curves for osmose and swelling are not quantitatively comparable, as the substances used are not identical. Also, the liquid on the inside of the laminaria was not pure water, but contained dissolved material. Besides this there was a difference in the vol-

ume ratios of dilute and concentrated solution used in the swelling and osmose experiments which would tend to make a difference in the final results. It would seem, however, that conditions were nearly enough alike to warrant a qualitative comparison.

In general the osmose curves, when plotted as above, are the opposite of the swelling curves. That is, a negative osmotic tendency corresponds to a swelling effect, while a positive osmotic tendency corresponds to a shrinking effect.

Data and curves for the swelling of such substances as gelatin,<sup>12</sup> barley,<sup>13</sup> fibrin,<sup>13</sup> gluten,<sup>14</sup> sunflower seeds,<sup>15</sup> and protoplasm<sup>16</sup> are to be found in the literature. The similarity of the swelling curves for these widely different

<sup>12</sup> Hoagland, *Soil Science*, 3, 547 (1917).

<sup>13</sup> Fischer, *Pfluger's Arch.*, 125, 99 (1908).

<sup>14</sup> Upson and Calvin, *THIS JOURNAL*, 37, 1295 (1915).

<sup>15</sup> Borowikow, *Biochem. Z.*, 48, 236 (1913).

<sup>16</sup> Lloyd, *Trans. Roy. Soc. Canada*, [3] 11, 133 (1917).

substances would lead us to believe that the manner of swelling was similar in all cases. Different conditions and materials give the same general type of curve, but with maximum and minimum values coming at somewhat different concentrations. In all cases the swelling seems to increase with addition of acid or alkali up to a certain point, when it decreases again. The authors believe that a further study of anomalous osmose and its relation to the swelling of colloid materials should find important applications in various problems of biology; also in such every day problems as tanning, the preservation of fruits, meats, etc.; in fact in all problems in which the direction of flow of solutions through membranes cannot be predicted from a knowledge of the isotonic values of the solutions concerned.

ANN ARBOR, MICHIGAN.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, CORNELL UNIVERSITY.]

### GERMANIUM. III. GERMANIUM TETRABROMIDE AND GERMANIUM TETRACHLORIDE.<sup>1</sup>

BY L. M. DENNIS AND F. E. HANCE.

Received December 5, 1921.

#### Germanium Tetrabromide.

Winkler<sup>2</sup> prepared what he assumed to be germanium tetrabromide by heating germanium in vapor of bromine, and also by heating a mixture of pulverized germanium and mercuric bromide. He stated the product to be a mobile, fuming liquid which solidified at 0° or slightly below that temperature to a white crystalline mass. He did not analyze or make a detailed study of the compound because of lack of material.

The present investigation describes the preparation and further study of this substance.

**Material.**—Germanium was prepared in finely divided form by reducing<sup>3</sup> germanium dioxide in a current of hydrogen at temperatures between 550° and 600°. Toward the end of the reduction the temperature was raised to 900°.

Bromine was purified by first digesting it with calcium bromide and zinc oxide,<sup>4</sup> then distilling the bromine, converting the middle fraction to hydrobromic acid by treating it with sulfur dioxide in the presence of water, distilling the hydrobromic acid, and liberating the bromine from this by means of pure manganese dioxide. This bromine was redistilled, was next dried over phosphorus pentoxide, and was then again distilled. The middle fraction was used.

**Preparation of Germanium Tetrabromide.**—Powdered germanium was placed in aluminum boats which were inserted in a tube of Jena glass lying in an electric combustion furnace. A thermometer was laid in the combustion tube beside the boats.

<sup>1</sup> The investigation upon which this article is based was supported by a grant from the Heckscher Foundation for the Advancement of Research, established by August Heckscher at Cornell University.

<sup>2</sup> Winkler, *J. prakt. Chem.*, **144** (N. S. 36), 193(1887).

<sup>3</sup> Further details concerning this reaction will be given in a later article.

<sup>4</sup> Richards and Merigold, *Proc. Am. Acad. Arts Sci.*, **37**, 387 (1901-2).



To the front end of this tube was attached an inverted T-tube. The upright arm of the T-tube was sealed to a separatory funnel containing bromine. The further end of the T-tube was joined to a chain of apparatus supplying purified nitrogen. The exit end of the combustion tube was brought well within a long adapter which in turn was fused to the inlet tube of the first of 2 small, all-glass distilling bulbs.<sup>5</sup> The side arm of the second bulb was connected with a U-tube containing calcium bromide, and this to a water suction-pump and manometer.

In beginning the procedure, nitrogen was started flowing slowly through the apparatus. Slightly diminished pressure was maintained throughout the run by suitable adjustment of the suction pump. When the whole apparatus was filled with nitrogen, bromine was slowly admitted into the T-tube. A small alcohol lamp placed beneath this tube hastened the volatilization of the bromine. A freezing mixture of ice and salt was brought up around the bulb that served as the first receiver.

Reaction between the bromine and germanium began at once in the unheated tube (26°), small, colorless globules of oily liquid appearing on the inner surface of the tube. Combination of the two elements apparently ceased after a short time, and vapor of bromine passed over into the receiver. The temperature of the tube was then slowly raised. At 180° slow union again was discernible. At 220° germanium bromide was rapidly produced, and it was found that bromine could now be admitted at the rate of 20 drops per minute without any appreciable amount of it escaping combination with the germanium. The temperature was maintained at 220° until the interaction apparently had ceased and free bromine appeared in the receiver. During the experiment, an oily liquid had steadily passed over, and had collected entirely in the first of the receiving bulbs. The admission of bromine was now stopped and the apparatus was allowed to cool in the current of nitrogen. During this interval the distillate in the cooled receiver solidified to a yellowish-white solid.

There remained in the alundum boats a grayish-white residue which proved to be chiefly germanium dioxide. The reasons for its occurrence here will be discussed in a later article.

The flask containing the distillate was disconnected from the chain, a U-tube filled with calcium bromide was attached to the side-arm, and the neck of the flask was tightly stoppered. The contents was warmed until it melted, and about 2 cc. of mercury was then introduced. Agitation of the flask soon removed the free bromine, and the supernatant liquid became clear and colorless. Later analysis showed that the product is germanium tetrabromide. Before making the analysis to establish its identity, the liquid was purified by fractional distillation and its boiling point was determined.

The germanium tetrabromide was siphoned from the mercury into a dry distilling flask, the substance being carefully protected from moisture during the transfer. It was then twice distilled, but a sample of the second distillate showed on spectroscopic examination the presence of a slight amount of mercury. For this reason a second preparation of the germanium tetrabromide was made, and from this the free bromine was removed by repeated fractional distillation instead of by the use of mercury. A large middle fraction that passed over at about 183° was then used for the determination of the boiling point and 71 readings, taken at 1-minute intervals, gave a constant boiling point of 183.0°, the total weight of the germanium tetrabromide that distilled over at this temperature being 97.47 g. The corrected boiling point was then calculated according to the formulas given by Young.<sup>6</sup> There is no formula that is generally applicable to the accurate correction of the observed boiling point to that under standard

<sup>5</sup> See Dennis and Bridgman, *THIS JOURNAL*, 40, 1543, Fig. 5 (1918).

<sup>6</sup> Young, "Fractional Distillation," MacMillan and Co., 1903, pp. 12, 14.

pressure. Young states that quite precise results are, however, obtained by the use of the formula  $\Theta = K(760 - P) (273 + t)$ . Provided the value of the constant  $K$  is determined experimentally,  $\Theta$  is the correction in centigrade degrees to be added to the observed boiling point  $t$ , and  $P$  is the barometric pressure corrected to 0°. Young gives the value of  $K$  for several substances among which are silicon tetrachloride and tin tetrachloride. He further states that the value of the constant is not altered by replacing one halogen by another. Inasmuch as germanium lies between silicon and tin in the fourth group of the periodic table, the value of  $K$  for germanium tetrachloride and germanium tetrabromide may be assumed to lie midway between the value for silicon tetrachloride, 0.000126, and that for tin tetrachloride, 0.000121. The boiling point of germanium tetrabromide thus corrected is 185.9°.

**Analysis.**—Portions of about 2 g. each of the substance were introduced into small glass capsules of known weight and the capsules were then sealed and weighed again. A capsule was broken under absolute alcohol and the solution was diluted to 250 cc. with absolute alcohol. Two portions of this solution were used for the analyses. The bromine was determined by precipitation as silver bromide. The filtrate was freed from silver by the addition of hydrobromic acid in very slight excess. The silver bromide was filtered off, conc. hydrochloric acid was added to the filtrate until the acidity was 6 *N* and the germanium was then precipitated by hydrogen sulfide. The germanium sulfide was washed with alcohol, was then oxidized with nitric acid, was ignited at red heat to constant weight, and was weighed as germanium dioxide.

In calculating the results of the analyses, 72.5 was used as the atomic weight of germanium.

Wt. of GeBr <sub>4</sub>		Wt. of Ge		Wt. of Br	
G.	Calc.	Found	Calc.	Found	G.
0.2158	0.0398	0.0403	0.1759	0.1753	
0.2158	0.0398	0.0399	0.1759	0.1756	

The results of the analyses, while not in very close accord with those calculated, suffice to establish the identity of the substance as germanium tetrabromide.

**Melting Point.**—About 90 g. of germanium tetrabromide of constant boiling point was brought into a large test-tube and its melting point was determined with the aid of an Anschütz thermometer that had been calibrated by the Bureau of Standards. The observed melting point was 26°. The corrected melting point was 26.1°.

**Crystal Form.**—A crystallographic examination of the substance was kindly made for us by Professor A. C. Gill of the Department of Mineralogy. Inasmuch as the substance could not be exposed to the air during observation under the microscope, a sample of about 1 cc. was sealed in a thin-walled glass tube and was cooled therein until it crystallized. The crystals were found to be brilliant, white, flattened octahedrons which

under polarized light proved to be isotropic, indicating that they belong to the regular system.

**Index of Refraction.**—An approximate determination of the index of refraction was first made using a microscope, Abbe condenser, and graduated screen. The germanium tetrabromide was placed in a small brass cell that was mounted on a cover glass. The cell was first calibrated with water, oil of cedar, and oil of cassia. The approximate value for the refractive index thus obtained was 1.61.

More accurate determinations of the index of refraction were then made with an Abbe refractometer. The super-cooling exhibited by germanium tetrabromide made it possible to obtain a series of readings at temperatures below the melting point of the substance.

Temperature °C.	Index of Refraction
20.75	1.6296
21.10	1.6292
22.20	1.6283
24.00	1.6274
24.50	1.6272
25.50	1.6268

Index of Refraction of Germanium Tetrabromide at 25° = 1.6269.

**Specific Gravity.**—A pycnometer of 10cc. capacity was dried over phosphorus pentoxide and was then quickly filled with germanium tetrabromide. The measurements were made at 29° to keep the substance in a liquid state. At this temperature,  $d_{29}^{29} = 3.1315$ .

**Electrical Conductivity.**—An alternating current, 1000 cycles per second, was used. Resistance was measured by a Wheatstone bridge with telephone attachment. A conductivity cell of 18cc. capacity and 90 mm. between platinum electrodes, was filled with germanium tetrabromide and was at once sealed to prevent contact with the moisture of the air. The cell was placed in a bath that was maintained at a constant temperature of 30°. A resistance totaling 300,000 ohms was found to be insufficient to balance the resistance of the cell. This shows that the specific conductivity of germanium tetrabromide is less than 0.000078 mho.

**Chemical Properties.**—In the liquid form germanium tetrabromide is a colorless, mobile liquid which fumes when brought into contact with the air. It shows to a marked degree the property of super-cooling, and it was found that the liquid when not agitated could be chilled to a temperature of  $-18^{\circ}$  before it solidified. The substance crystallizes in minute, white octahedrons. This crystalline mass gradually changes on standing into a clear, hard, transparent, glass-like material with fractures running through it like the fissures in a lump of cracked glass.

When a few drops of water were added to about 1 cc. of liquid germanium tetrabromide, hydrolysis at once took place with the evolution of heat. A layer of hydrated germanium dioxide formed at the surface, and if the tube was not agitated, two liquid layers appeared below this solid crust. The lower layer consisted of unchanged germanium tetrabromide and the upper layer of a suspension of germanium hydroxide.

When a drop of germanium tetrabromide was allowed to fall into water, a small, white ring of hydrated germanium dioxide was formed and further deposit of the white hydroxide around the circumference of this ring rapidly built up.

In one experiment 25 g. of germanium tetrabromide was poured into 50 cc. of water. The tetrabromide sank to the bottom of the tube, and at the surface of contact between the two liquid layers there was rapidly formed a heavy film of germanium hydroxide. Above this film there gradually appeared a fine suspension of this substance. The layer of germanium hydroxide protected the tetrabromide below it from further hydrolysis for more than 24 hours, the hydroxide forming a tough impervious stratum. The water above this layer of germanium hydroxide gradually cleared and this clear solution gave a decided acid reaction to litmus. When germanium tetrabromide is dropped into water, there is noted a slight but distinct crackling sound. It is scarcely audible and it would probably have escaped attention were it not for the fact that a similar phenomenon had already been noticed when germanium tetrachloride and water are brought together.

When a few drops of germanium tetrabromide were allowed to fall into 2 cc. of conc. sulfuric acid, the substance sank to the bottom of the tube and no reaction nor visible change took place during the several days that the tube was allowed to stand at room temperature. This behavior is similar to that of the tetrachlorides of tin and lead, elements which lie below germanium in Group 4 of the Periodic Table.<sup>7</sup>

When germanium tetrabromide was introduced into an aqueous solution of potassium hydroxide (1:4), reaction took place at once with the evolution of heat. Germanium hydroxide first separated and then quickly dissolved in the alkali. When carbon dioxide was passed through this solution of potassium germanate, a heavy white precipitate resulted.

When germanium tetrabromide was dropped into conc. nitric acid, it fell to the bottom of the tube and gradually became deep orange in color. The nitric acid above the tetrabromide became yellow and turbid and was rapidly reduced. The layer of germanium tetrabromide soon became dark brown in color and a disk of white germanium oxide formed between the two liquid layers. After about 15 minutes the color of the tetrabromide changed to black and the reaction between it and the nitric acid went on

<sup>7</sup> Friedrich, *Ber.*, 26, 1434 (1893).

slowly with copious evolution of nitric oxide. After the reaction had ceased, water was added to the contents of the tube whereupon there formed a precipitate that appeared to consist of white powder, a yellowish substance, and the black amorphous precipitate previously mentioned. The supernatant liquid was clear and of a pale yellow color. After standing for 24 hours, the precipitate in the bottom of the tube became entirely white.

With dry ammonia, germanium tetrabromide formed a white solid compound which is probably analogous to the corresponding compounds of ammonia with the tetrabromides of silicon and tin. This substance is now being subjected to further study.

Germanium tetrabromide was found to be soluble in absolute alcohol, carbon tetrachloride, benzene, and ether without decomposition. It dissolves in acetone but slow decomposition takes place with the liberation of bromine.

### Germanium Tetrachloride.

Germanium tetrachloride was first prepared<sup>8</sup> by Clemens Winkler in 1886. He found its specific gravity to be 1.887 at 18°, its boiling point 86°, and he adds that it did not solidify at -20°. In our investigations upon the compounds of germanium with the halogens, it seemed desirable to redetermine the above constants of germanium tetrachloride and to study somewhat further the properties of the compound.

**Preparation.**—In the preparation of germanium tetrabromide by the action of bromine upon germanium that had been prepared by the reduction of germanium dioxide in hydrogen, the very considerable residue of germanium dioxide that remained after action between the metal and bromine had ceased, showed that reduction of germanium dioxide by hydrogen is difficult to carry to completion when fairly large quantities of the oxide are employed. In the preparation of germanium tetrachloride, a large yield was obtained by employing crystalline, fused germanium<sup>9</sup> that had been pulverized and thoroughly freed from any adhering flux.

This metallic germanium was heated in a current of chlorine in an apparatus quite similar to that used for the preparation of germanium tetrabromide, except that the lower boiling point of the tetrachloride rendered necessary a modification of the condensing tube. This was given the shape of a U-tube, to the bend of which there was fused a short tube that terminated in a bulb of about 60cc. capacity. The condensed germanium tetrachloride flowed down into this bulb and evaporation of the liquid by the nitrogen and chlorine flowing through the apparatus during the run was thus greatly lessened.

<sup>8</sup> Winkler, *J. prakt. Chem.*, 142 (N. S. 34), 177 (1886).

<sup>9</sup> The manner of its preparation will be described in a later article.

About 30 g. of pulverized germanium was placed in boats in the combustion tube. Purified nitrogen was then passed through the apparatus. A freezing mixture of ice and salt was packed around the U-tube condenser, the current of nitrogen was turned off, and dry chlorine that had been freed from vapor of sulfuric acid by passage through glass wool was then passed through the apparatus. The temperature of the electric combustion furnace was gradually raised. Reaction between the germanium and chlorine began at about  $80^{\circ}$ , and at  $180^{\circ}$  there was rapid combination of the two elements, although the heat of formation of the chloride did not bring the metal to incandescence. When the temperature was raised to  $360^{\circ}$ , near the end of the experiment, the metal glowed brilliantly when the chlorine was rapidly passed through the tube.

The germanium tetrachloride was completely condensed in the U-tube. The yield was about 45 cc. A very slight reddish-brown residue remained in the porcelain boats. The passage of chlorine was now discontinued, and nitrogen was run through the apparatus while it cooled.

It was found impracticable to free the germanium tetrachloride from chlorine by fractional distillation. Five fractionations gave a final product that still contained some free chlorine. The chlorine was removed by placing the tetrachloride in a distilling flask that had a long neck that was constricted at its lower end and was provided with a side-arm close to its upper end. A cork in the neck carried a glass tube that reached downward into the liquid. The space between this tube and the wall of the neck of the flask was tightly packed with glass wool. The neck of the flask was cooled by a refrigerant on the outside to prevent volatilization of germanium tetrachloride. The side-arm of the flask was joined to a condenser, and this connected to a U-tube that was packed in a freezing mixture. Upon passing dry air through the liquid at room temperature for 7 hours, it was found that the germanium tetrachloride had been freed from chlorine and that only a very small amount of the tetrachloride had been carried over through the condenser.

The residual germanium tetrachloride was then fractionally distilled from the flask. The bulk of the product passed over between  $85.2^{\circ}$  and  $85.8^{\circ}$ , and a large middle fraction was obtained that showed a constant boiling point of  $85.6^{\circ}$ . This fraction was redistilled and all but a trace of residue passed over at  $85.6^{\circ}$ . The corrected<sup>10</sup> boiling point of germanium tetrachloride is  $86.5^{\circ}$ .

**Analysis.**—Known amounts of the substance were sealed off in glass capsules. A capsule was broken under absolute alcohol, the solution was diluted with alcohol to 100 cc, and separate portions of this solution were used for the determination of chlorine by precipitation with silver nitrate, and for that of germanium with hydrogen sulfide.

Wt. of $\text{GeCl}_4$		Wt. of Ge		Wt. of Cl	
G.	Calc.	Found	Calc.	Found	
G.	G.	G.	G.	G.	G.
0.04289	0.0145	0.0144	.....	.....	
0.04289	0.0145	0.0145	.....	.....	
0.1972	.....	.....	0.1304	0.1301	
0.1970	.....	.....	0.1303	0.1303	

The analysis identifies the substance as germanium tetrachloride.

**Melting Point.**—A preliminary determination with a pentane thermometer gave  $-49^{\circ}$  as the melting point of the compound. The constant

<sup>10</sup> See p. 300.

was then accurately determined under the direction and with the assistance of Professor C. C. Bidwell of the Department of Physics, and we take pleasure in expressing here our appreciation of his kindly coöperation.

The determinations were made with a gold resistance thermometer, the resistance being measured by the fall of potential method. The instrument was calibrated against the boiling points of sulfur and water, the ice point, and the freezing point of mercury.

A test-tube was filled with pure germanium tetrachloride to a depth of 8 cm. which sufficed to completely immerse the thermometer. A larger test-tube was brought up around the smaller one to protect the latter from direct contact with the refrigerating agent, liquid air, and to avoid too rapid rise of temperature of the frozen samples after the liquid air was removed.

The melting point of germanium tetrachloride was found to be  $-49.5^{\circ} \pm 0.2^{\circ}$ .

**Index of Refraction.**—The measurement was made with an Abbe refractometer, and the index of refraction at  $27^{\circ}$  was found to be 1.3606.

**Specific Gravity.**—A pycnometer of 25cc capacity was thoroughly dried and was filled with germanium tetrachloride in a dry atmosphere;  $d_{25}^{25} = 1.874$ .

**Chemical Properties.**—Germanium tetrachloride is a colorless, mobile liquid that fumes strongly when brought into contact with the air. Our observations of the behavior of germanium tetrachloride when brought into contact with water, are substantially identical with those of Winkler.<sup>8</sup> Of peculiar interest is the crackling sound that is emitted when the two substances interact. If the container is not shaken, this snapping persists for hours, and can be heard at a distance of 2 meters.

When germanium tetrachloride is dropped into conc. sulfuric acid of room temperature, it sinks to the bottom of the tube and is not attacked by the acid even on long standing.<sup>11</sup>

Germanium tetrachloride reacts violently with a 1:4 solution of potassium hydroxide, the heat of reaction causing the distillation of some of the tetrachloride before interaction is complete. The germanium dioxide that forms and dissolves in the excess of the reagent is precipitable by carbon dioxide.

When germanium tetrachloride is dropped into conc. nitric acid, it sinks to the bottom and slow reduction of the acid takes place at the surface of contact between the two liquids. The tetrachloride becomes yellow in color but remains clear. Vigorous agitation somewhat hastens the reaction, but does not cause immediate decomposition of the tetrachloride. When the container is not shaken, a considerable portion of the tetrachloride still remains unattacked after 48 hours. Upon dilution

<sup>11</sup> See also H. Friedrich, *Monatsh.*, **14**, 505 (1893).

of the acid with half its volume of water, however, a slow but steady decomposition of the tetrachloride ensues.

When ammonia is passed into germanium tetrachloride, much heat is evolved and a white precipitate is formed. This substance is now being subjected to further study.

Germanium tetrachloride is soluble in absolute alcohol, carbon disulfide, carbon tetrachloride, benzene, chloroform, and ether. It dissolves in acetone with the formation of a light orange colored liquid.

### Summary.

This article deals with the preparation and purification of germanium tetrabromide and germanium tetrachloride, the analyses determination of the boiling points, melting points, indexes of refraction, specific gravities, and some of the chemical properties of the two compounds, and the crystal form and electrical conductivity of germanium tetrabromide.

ITHACA, NEW YORK.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NEW HAMPSHIRE COLLEGE.]

## THE ATOMIC WEIGHT OF YTTRIUM.

BY H. C. FOGG AND C. JAMES.

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This work was undertaken because the atomic weight of yttrium, the commonest member of the yttrium earths, varies considerably according to the results published by different workers. Among the publications concerning this work only those which appear to the writers to be of major importance are discussed below.

Clève<sup>1</sup> carefully purified yttria, first by means of the basic nitrate method, and finally by fractionally precipitating the oxalate from very acid solutions of the nitrate in order to remove the last traces of terbium. He found, as a result of 12 determinations by the synthesis of the sulfate, the value 89.12.

Jones<sup>2</sup> used yttrium oxide, very carefully purified by the sodium sulfate method to remove members of the cerium group and then by the ferrocyanide method to throw out erbium, etc. His ratio of yttrium oxide to sulfate gave an atomic weight of 88.96 as a mean of 10 determinations. A second series in which the sulfate was converted to oxide, yielded the value 88.98 as the average of 10 analyses.

Feit and Przibylla<sup>3</sup> by means of a volumetric method obtained 89.346 as a mean of 6 runs.

Meyer and Wuorinen<sup>4</sup> roughly separated the yttrium and cerium earths

<sup>1</sup> Clève, *Compt. rend.*, 95, 1225 (1882).

<sup>2</sup> Jones, *Am. Chem. J.*, 14, 154 (1895).

<sup>3</sup> Feit and Przibylla, *Z. anorg. Chem.*, 50, 262 (1906).

<sup>4</sup> Meyer and Wuorinen, *ibid.*, 80, 7 (1913).



by the use of sodium sulfate. The yttrium earths were then further purified by two new methods: (a) the fractional hydrolysis of the phthalates; (b) the precipitation as the iodate from dil. nitric acid solution. By synthesis of the sulfate they obtained 88.71 and 88.73. Later Meyer and Weinheber<sup>5</sup> working with material that had been extensively purified by the iodate method, obtained the values 88.75 as a mean of 6 determinations using the sulfate to oxide ratio, and 88.76 as a mean of 3 experiments involving the oxide to sulfate ratio.

Hopkins and Balke<sup>6</sup> purified their yttrium oxide by first submitting it to a series of crystallizations of the bromates, followed by the fractional precipitation of the basic nitrate by means of sodium nitrite. The results obtained from 6 runs of the oxide-to-chloride ratio gave an average of 88.91. Later Kremers and Hopkins<sup>7</sup> using the same material, studied the ratio of yttrium chloride to silver. As an average of 7 results they obtained the value 89.33.

With the exception of the last three sets of results, those given above were obtained from the sulfate-to-oxide ratio or *vice versa*. These processes have been justly criticized by various workers from time to time, as can be ascertained by reference to previous papers upon the subject. Of the three remaining sets, only one, the last, involves the use of a standard method, namely, the chloride-to-silver ratio.

### The Extraction of Yttrium Oxide.

The material used in this work was derived entirely from Norwegian gadolinite in the following manner.

The mineral was finely powdered, decomposed by heating for some time with an excess of 1:1 commercial hydrochloric acid, diluted with water, filtered and precipitated warm with a hot solution of oxalic acid. The washed and dried oxalates were converted into sulfates by heating with conc. sulfuric acid until white fumes ceased to be evolved. The sulfates were dissolved in cold water in a large copper tank provided with a mechanical stirrer. The resulting solution, which was not completely saturated, was poured over an excess of barium bromate, gently warmed, and well stirred. As soon as the decomposition was complete, the solution was removed by filtration. The residue, which consisted of barium sulfate and barium bromate, was treated with more rare earth sulfate solution. When an excess of sulfate ions was found to be present after long heating and stirring, it was concluded that practically all the barium bromate had been exhausted. The solution was removed from the barium sulfate and the latter well washed. The filtrate and wash water were then poured over a new lot of barium bromate. The mixture was gently heated and well stirred, as before, until no test for a sulfate could be obtained. The filtered liquid was then added to the former bromate solution and the processes repeated until all the rare earth sulfate was converted to bromate.

**Crystallization of the Bromates.**<sup>8</sup>—The bromates were then submitted to a long

<sup>5</sup> Meyer and Weinheber, *Ber.*, 46, 2672 (1913).

<sup>6</sup> Hopkins and Balke, *THIS JOURNAL*, 38, 2332 (1916).

<sup>7</sup> Kremers and Hopkins, *ibid.*, 41, 718 (1919).

<sup>8</sup> *THIS JOURNAL*, 30, 182 (1908).

series of fractional crystallizations. As the fractionation progressed, the erbium absorption spectrum began to fade in the least soluble, while that of thulium appeared in the most soluble fractions. When the erbium bands had completely disappeared from the least soluble fractions, they were removed from the series. When strong thulium bands appeared in the most soluble fractions, these were mixed together and set aside. After the work had continued for a considerable time, the absorption bands of the middle fractions gradually became weaker. When it became apparent that the material consisted mainly of yttrium, the fractionation was discontinued and the fractions divided into two sets, namely, (a) yttrium bromate with some holmium and dysprosium, and minute amounts of erbium; (b) yttrium bromate containing a very little erbium and practically no holmium.

Since yttrium is more easily separated from erbium than from holmium, the latter set (b) was selected for the continuation of the work, in which stage it was decided to employ the basic nitrates.

**Precipitation as Basic Nitrates.**<sup>9</sup>—The bromates were boiled with an excess of sodium hydroxide solution until thoroughly decomposed. The hydroxides were filtered off, washed with boiling water, and dissolved in nitric acid. The concentrated solution of nitrates was boiled and treated with dil. sodium hydroxide solution until minute crystals could be observed swirling through the liquid. The vessel was then removed from the burner and allowed to stand for 24 hours. The precipitate of basic nitrate which formed was filtered off and the filtrate treated with more dil. sodium hydroxide solution as above until several fractions had been obtained. The precipitates were dissolved in the least quantity of nitric acid and fractionated in the same manner. Whenever filtrates or solutions of precipitates appeared from their absorption spectra to have the same earth content, they were united. As soon as nearly all the erbium had been removed, which was shown by the bands becoming faint, the yttrium was precipitated in the form of the oxalate and stored until 6 or 8 kg. had been collected.

**Precipitation as Basic Nitrate by Means of Sodium Nitrite.**<sup>10</sup>—During this stage very slow precipitation was brought about by boiling dilute neutral nitrate solutions with sodium nitrite. The sodium nitrite was added in small amounts at a time and the boiling continued until the precipitate was considered sufficiently large. This was immediately filtered off and the liquid subjected to fractionation in the above manner until nearly all the yttrium had been removed, after which the liquid was rendered slightly acid with nitric acid and precipitated with oxalic acid. Each basic nitrate precipitate was dissolved in the least quantity of nitric acid, the solution diluted, neutralized with dil. sodium hydroxide solution while boiling, and further fractionated with sodium nitrite. Any fractions which appeared to be similar after a careful examination by the spectroscope were united. During this fractionation the purest yttrium, which collected in the last or most basic fractions, was placed aside when the absorption bands of erbium were scarcely discernible.

**Fractional Precipitation as the Ferricyanide.**<sup>11</sup>—Two hundred g. of oxide derived from the above nitrite fractionation was dissolved, carefully, in the least possible quantity of nitric acid, diluted to 2 liters and rendered neutral by the addition of a dilute solution of sodium hydroxide to the boiling liquid. Two hundred cc. of a 20% solution of potassium ferricyanide was added drop by drop while the whole was well stirred by a rapid current of steam. The volume of the solution in the flask was kept constant by the application of outside heat. After the potassium ferricyanide had been added, the liquid was kept boiling until the desired quantity of precipitate had formed. The

<sup>9</sup> THIS JOURNAL, 43, 1397 (1921).

<sup>10</sup> *Ibid.*, 36, 1419 (1914).

<sup>11</sup> *Ibid.*, 39, 936 (1917).

red crystalline precipitate of ferricyanide was immediately filtered off, the liquid returned to the flask and the process repeated until 6 fractions had been obtained. The remaining yttrium which constituted Fraction 7 was removed by the addition of an excess of sodium hydroxide solution. A similar run was made employing 250 g. of yttrium oxide.

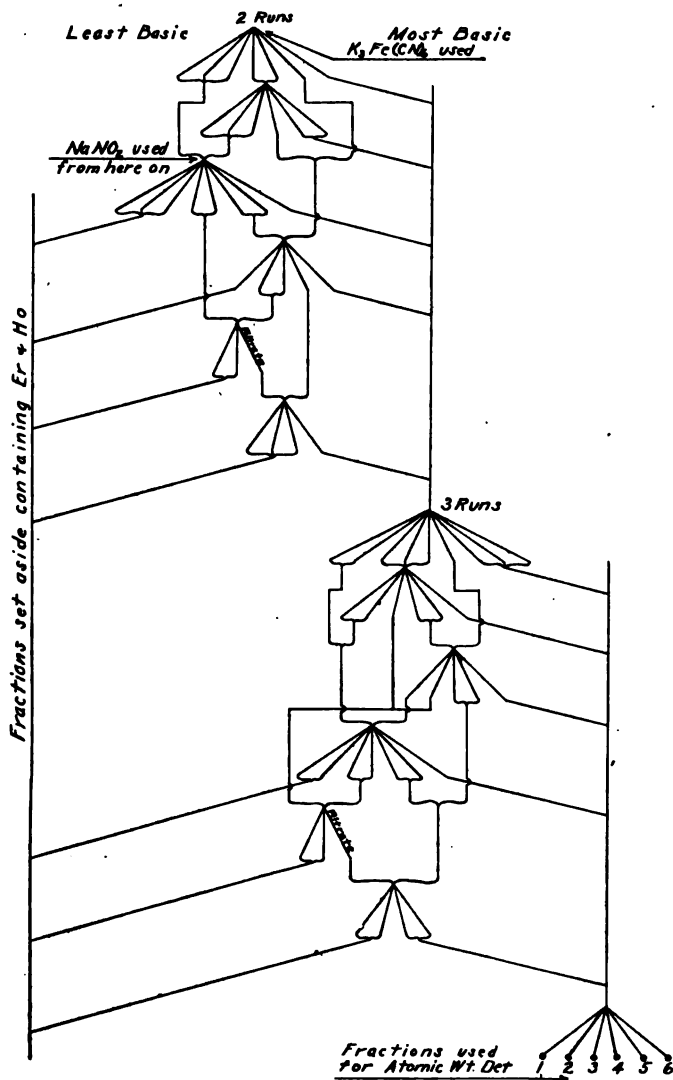


Fig. 1.

The precipitates were converted back to nitrates in the following manner. After being transferred to porcelain casseroles, they were boiled with an excess of conc. sodium hydroxide solution until decomposed, as shown by the disappearance of the red color. The residues were filtered off, washed and ignited. The resulting oxides were transferred to beakers, moistened with water, dissolved in conc. hydrochloric acid and

evaporated nearly to dryness in order to expel the excess of acid. The chlorides were taken up with approximately 400 cc. of water, heated to boiling and precipitated as the oxalates. After standing for several hours the precipitates were removed by filtration, ignited to oxide, transferred to beakers, dissolved in nitric acid, evaporated to sirupy consistency, examined with a spectroscope and divided into 4 groups according to purity, namely, (a) Fractions 1, 2 and 3 from each series; (b) Fractions 4 and 5 from each series; (c) Fraction 6 from each series; (d) Fraction 7 from each series.

Group b was fractionated as before, taking 5 fractions with potassium ferricyanide and the last (No. 6) with sodium hydroxide. The precipitates were converted back to nitrates as in the previous case, and the fractions placed in the following groups: (e) Fractions 1, 2, and 3; (f) Fraction 4; (g) Fractions 5 and 6. Group e was then united with Group a; Group f with c; and Group g with d. This will be better understood by referring to the diagram.

Owing to the fact that the conversion of the ferricyanide to the nitrate was troublesome, and since the separation was no better than in the case of the sodium nitrite method, the latter was resorted to from this point on. The fractionation was therefore continued in a similar manner to the above except that 200 cc. of a 20% solution of sodium nitrite was used in place of potassium ferricyanide, and the precipitates converted back to nitrate by dissolving in the least amount of nitric acid. The work was carried through two stages, the purest material obtained in the first stage, which showed an extremely faint holmium band when examined through a thick layer of fused nitrate, being subjected to a similar process. The purest fractions obtained from this, which failed to give the slightest evidence of absorption bands of erbium or holmium, were united, and the whole broken up into 6 fractions as nearly equal as possible, by the above method.

During the fractionation it was observed that the most basic fractions gave a light cream colored oxide upon ignition, which was proved to be due to praseodymium, as will be shown later.

**Composition of the Precipitate Obtained during the Nitrite Fractionation.**—This precipitate consisted of small, transparent, hexagonal plates, which after ignition gave an oxide having the same transparent crystalline appearance. A careful analysis of the material from two different fractions gave 63.54 and 63.44% of  $Y_2O_3$ , 14.93 and 14.77% of  $N_2O_5$  and 21.53 and 21.79% of  $H_2O$  (by difference). This composition corresponds to a compound possessing the formula  $4Y_2O_3 \cdot 2N_2O_5 \cdot 17H_2O$ . A very small amount of nitrous anhydride was present and this was calculated and included as nitric anhydride. This nitrite content varied among the different fractions, so the writers assumed that it was merely occluded. A slight difference in the amount of water present would simplify the formula, inasmuch as it could be  $2Y_2O_3 \cdot N_2O_5$  with 8 or 9  $H_2O$ .

The ratio  $Y_2O_3 : N_2O_5$  in this case is different from the ratio of the basic nitrate<sup>12</sup>  $3Y_2O_3 \cdot 4N_2O_5 \cdot 20H_2O$ . A study of the figures given on pages 877 and 878 of this reference indicates that there is a possibility that this more basic nitrate may exist at 25° and lie along the portion of the curve AB.

**Purification of the Yttrium Material.**—As previously mentioned it had been noticed that some of the most basic fractions gave an oxide which possessed a pale cream color. It was therefore obvious that a minute amount of an element giving a dark colored oxide must be present, *i. e.*, praseodymium or terbium or both. Since the yttrium material had been submitted to a very long series of fractional crystallizations of the bromates, it was highly probable that all terbium had been removed, inasmuch as

<sup>12</sup> THIS JOURNAL, 32, 873 (1910).

terbium bromate is one of the least soluble rare earth bromates. This leaves praseodymium as the other alternative. If this were so, there would also be the possibility of the presence of lanthanum, since this element gives a very soluble bromate and in addition a strongly basic oxide.

A search was then made for suitable compounds showing a great divergence between the solubilities of yttrium and the most basic cerium earths. In order to make the process thoroughly efficient, it was necessary that the salts of the cerium earths be much more soluble than that of yttrium. The following compounds seemed to offer the best possibilities: (a) dimethylphosphates, (b) acetates, (c) *p*-sulfobenzoates, and (d) cacodylates.

**Dimethylphosphates.**<sup>13</sup>—Fraction 1 which was in the form of nitrate, was precipitated by oxalic acid, the oxalate washed, ignited and the resulting oxide dissolved in acetic acid. The excess of acid was neutralized by ammonium hydroxide, the whole heated to boiling and a hot neutral solution of ammonium dimethylphosphate added. The voluminous precipitate of yttrium dimethylphosphate was removed by filtration and washed with hot water. Two more fractions were obtained in like manner from the filtrate. The yttrium remaining in the mother liquor was thrown out as the oxalate. The colors of the oxides of the various fractions indicated that there had been no concentration of the earth with the colored oxide. A duplicate run confirmed these results.

**Acetates.**<sup>14</sup>—The oxide from Fraction 6 was dissolved in acetic acid and submitted to 31 series of fractional crystallizations. While this method concentrated the colored earth in the mother liquors, it was found to be too wasteful and tedious.

***p*-Sulfobenzoates.**—The writers found that there was a considerable difference between the solubilities of the yttrium *p*-sulfobenzoates and those of the cerium earths. However, the fractionation of these salts failed to bring about any separation in this case. This subject is to be investigated at greater length in the near future.

**Cacodylates.**<sup>15</sup>—The mother liquors from the acetate crystallization of Fraction 6, which gave a chamois colored oxide, were evaporated to dryness to remove excess of acid, taken up with water and precipitated by means of ammonium cacodylate. The rare earth remaining in solution was precipitated as the oxalate. After both fractions had been converted to oxide, a great difference in color was immediately observed, the oxide from the precipitate being practically white, while that from the filtrate was a deep chocolate color. A solution of the latter in nitric acid showed weak praseodymium absorption bands. Since lanthanum cacodylate has never been obtained in a crystalline form, it was concluded that lanthanum would be found with the praseodymium in the filtrate. Inasmuch as the above results show that small amounts of praseodymium (and lanthanum) are rapidly removed from yttrium by precipitating the latter as cacodylate from acetate solution, this procedure was employed for the final purification.

<sup>13</sup> THIS JOURNAL, 36, 10 (1914).

<sup>14</sup> Postius, *Dissertation*, München Polytech., 1902, pp. 11–30.

<sup>15</sup> THIS JOURNAL, 35, 127 (1913).

Each fraction was converted to oxide, dissolved in acetic acid, evaporated almost to dryness to remove excess of acid, taken up with water and diluted to 250-300 cc. The solution was then heated to boiling and treated with a slight excess of ammonium cacodylate. After a few minutes' heating and stirring a voluminous, crystalline precipitate formed. This precipitate was removed by filtration, washed, transferred to the original beaker, suspended in water and dissolved in a slight excess of acetic acid. When solution was complete, 5 to 10 g. of cacodylic acid was added, and the liquid boiled. At this point dil. ammonium hydroxide was added with thorough stirring until an odor of ammonia was perceptible. When this procedure was carefully carried out only a slight amount of rare earth was found to remain in solution. The precipitate was again removed by filtration and the process repeated one precipitation beyond the stage where a white yttrium oxide was obtained from the filtrate, in order to make sure that all the cerium earths were removed. The number of precipitations required varied from 3 to 6.

#### The Preparation of Yttrium Chloride.

Each final cacodylate precipitate was dissolved in hydrochloric acid, diluted to about 3 liters, heated to boiling and precipitated by the addition of a hot dilute solution of oxalic acid. The whole was allowed to stand over night, washed several times by decantation with boiling water to which a little oxalic acid had been added, and then filtered upon a hardened paper placed on a perforated porcelain plate in a glass funnel. The oxalate was transferred from the paper to a porcelain dish and ignited in an electrically heated quartz muffle furnace. The oxide was dissolved in redistilled dil. hydrochloric acid, diluted to about 3 liters and reprecipitated as the oxalate. After filtering and washing, the precipitate was detached from the filter paper and ignited in a Palau dish at a dull red heat. The oxide was again dissolved in hydrochloric acid and precipitated for the third time as oxalate. The oxide resulting from the ignition of this last oxalate precipitation was dissolved in hydrochloric acid, the solution diluted to about 3 liters, treated with an excess of ammonium chloride and precipitated by means of redistilled ammonium hydroxide. The hydroxide was washed several times by decantation, placed on a Büchner funnel and again washed. This hydroxide was dissolved in hydrochloric acid and reprecipitated as above. The precipitate was redissolved in hydrochloric acid, diluted to about 3 liters, precipitated as the oxalate, and converted to oxide. This oxide was dissolved in hydrochloric acid, evaporated to small volume, transferred to a platinum dish and evaporated to dryness in a glass oven, after which it was heated to 110° for several hours. The residue was treated with water and acidified with dil. hydrochloric acid. The solution was carefully filtered, and the entire dehydration process repeated twice.

Some of the later dehydrations were carried out in the following manner. The chloride solution was evaporated in a platinum dish over a hot plate with constant stirring until it just became solid on cooling. The crystals were coarsely powdered, placed in a silica boat and carefully dehydrated in a current of pure dry hydrogen chloride, the temperature being gradually raised to 170–200°. The advantage of this method over the above is that the resulting dehydrated chloride is completely soluble in water, thus obviating the possibility of dissolving any silica by hydrochloric acid.

The solution of the chloride, resulting from the final dehydration, was diluted to about 200 cc. and treated with hydrogen sulfide, first in the cold and then boiling. No appreciable precipitate was obtained in any case, indicating that all arsenic had been previously removed. After filtration the liquid was diluted, heated to boiling and the oxalate precipitated by oxalic acid solution, filtered off, washed and gently ignited. The oxide was dissolved in dil. hydrochloric acid in a quartz dish and purified by two crystallizations of the chloride as follows. The solution was evaporated to the point of crystallization, cooled in ice and saturated with hydrogen chloride. The thick mass of crystals was transferred to a platinum Gooch crucible and the mother liquor removed by means of a centrifuge. The yttrium chloride obtained by the second crystallization was dried over fused potassium hydroxide in a vacuum desiccator.

#### The Preparation of Other Reagents.

The purification of the silver was described in an article upon the atomic weight of samarium.<sup>16</sup> The distilled water of the laboratory was further purified by two more distillations, first from alkaline permanganate and second from sulfuric acid, using tin condensers and well-seasoned Jena glass receiving flasks. The hydrochloric and nitric acids were twice distilled through quartz condensers, the first and last thirds being rejected.

#### The Dehydration of Yttrium Chloride.

Hydrated yttrium chloride,  $\text{YCl}_3 \cdot 6\text{H}_2\text{O}$ , melts at 156–160°, loses 5 molecules of water at 100° and the six at 160°, giving the anhydrous salt which melts at about 686°. <sup>17</sup> The dehydration was carried out in a similar manner to that employed by Baxter and his co-workers.<sup>18</sup> The hydrated salt was coarsely powdered in an agate mortar, transferred to a platinum boat and placed in the bottling apparatus. After the air had been swept out by nitrogen and hydrogen chloride, the temperature was raised to and kept at 100° for an hour or so, after which it was raised to 125° to 135°. When moisture had ceased to be evolved, the temperature was

<sup>16</sup> THIS JOURNAL, 39, 2609 (1917).

<sup>17</sup> Matignon, *Compt. rend.*, 134, 1308 (1902); *Ann. chim. phys.*, 8, 433 (1906).

<sup>18</sup> Baxter, THIS JOURNAL, 37, 516 (1915).

increased to 170–180°, when more water was given off. At 250° nitrogen was shut off and only hydrogen chloride passed through the apparatus. At 280–300° the last amount of water was driven off. After the salt had been kept at 325° for an hour the heater was removed, the apparatus allowed to cool and the hydrogen chloride removed by a current of nitrogen. The salt was removed, ground in an agate mortar, returned to the apparatus and heated to 300–350° for some time in a stream of hydrogen chloride, after which the temperature was quickly raised until the chloride fused. The heating sleeve was removed, the apparatus allowed to cool, the hydrogen chloride swept out by nitrogen and this in turn by air. The boat was then bottled and placed in a desiccator, which was set near the balance.

### Analysis.

The chloride, after weighing, was dissolved in about 200 cc. of water in a glass-stoppered Erlenmeyer flask, and then transferred to a 2-liter bottle where it was diluted to about 600 cc. All samples analyzed dissolved completely and quickly.

The silver, equivalent within a few tenths of a milligram to the yttrium chloride, was dissolved in dil. nitric acid in an Erlenmeyer flask fitted with a column of bulbs. When the oxides of nitrogen had been driven off, the solution was diluted to 250 cc. and added to the chloride solution with thorough mixing by rotation. The whole was kept, with frequent shaking, for at least 10 days and then tested nephelometrically, deficiency in either silver or chloride being made up by the addition of a solution of silver containing 1 g. per liter or from an equivalent solution of potassium chloride. When the solution was found to be nephelometrically equivalent, the bottle was allowed to stand with occasional shaking for a week or two and again tested to make sure that equilibrium had been reached. All weighings were made on a Staudinger balance and with weights reserved for this type of work. The weights were standardized by the method described by Richards.<sup>19</sup> The balance case contained, in addition to fused potassium hydroxide, radio-active material. The weighings were made by substitution using counterpoises almost exactly like the vessels themselves in size and weight. Vacuum corrections were applied as follows.

Material	Sp. Gr.	Vacuum corrections per g.
YCl <sub>3</sub>	2.80 <sup>a</sup>	+0.000287
Ag	10.49	−0.000031

<sup>a</sup> Matignon, *Ann. chim. phys.*, 8, 433 (1906).

<sup>19</sup> Richards, *This Journal*, 22, 144 (1900).



TABLE I

Analysis	Fraction	Wt. of YCl <sub>3</sub> in vac. G.	Wt. of Ag in vac. G.	At. wt. of yttrium
1	2	2.32881	3.85660	89.06
2	3	2.62838	4.35335	89.03
3	5	2.70726	4.48289	89.08
4	6	2.57431	4.26298	89.07
5	4	2.42924	4.02481	88.97
6	2	2.99852	4.96557	89.06
7	3	3.13897	5.19903	89.03
8	5	4.20721	6.96662	89.08
9	1	2.45615	4.06741	89.06
10	2	2.60321	4.31174	89.03
11	3	2.86276	4.74036	89.08
12	6	2.10381	3.48514	89.00
13	1	1.53281	2.53937	88.98
14	2	2.05579	3.40596	88.98
15	3	2.70410	4.47765	89.08
16	2	2.19335	3.63357	88.99
17	2	2.17992	3.61115	89.00
18	5	2.86866	4.75281	88.97
19	5	2.79189	4.62545	88.98
20	4	3.22857	5.34787	89.01
21	4	2.80721	4.64965	89.03
				Av. 89.03

### Summary.

It has been shown that in order to obtain very pure yttrium, it is essential to use, finally, such a method as the cacodylate in which the yttrium is precipitated, while the more basic cerium earths remain in the form of quite soluble salts.

The average atomic weight of 89.03, which agrees better with the average gravimetric analyses of yttrium salts, differs somewhat from the figure at present accepted by the International Committee.

The authors desire to express their appreciation to the committee of the Cyrus M. Warren fund for considerable assistance in this work.

DURHAM, NEW HAMPSHIRE.

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## THE CRYSTAL STRUCTURE OF POTASSIUM CYANIDE.

By RICHARD M. BOZORTH.<sup>1</sup>

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### I. Introduction.

The purpose of this research was to study by means of X-rays the crystal structure of potassium cyanide, hoping thereby to throw some light on the similarity in properties between this substance and the alkali halides. The crystallographic information is very meagre, nothing having been found in the literature except the statement<sup>2</sup> that the salt crystallizes from the melt in cubes and from an aqueous solution in octahedra.

This research was carried out in part with the aid of a grant made to Professor A. A. Noyes by the Carnegie Institution of Washington, for which I wish to express my indebtedness. I also wish to express my thanks to Dr. R. G. Dickinson, under whose immediate direction the work was carried out.

### II. Preparation of the Crystals and the Methods of Measurement.

The crystals used in this research were prepared by two methods. Slow evaporation of a saturated aqueous solution in a desiccator yielded crystals with (111) faces large enough for good spectrometer measurements. Cubes large enough for Laue photographs were formed by placing a layer of alcohol over the saturated aqueous solution and allowing diffusion to take place. After several days crystals formed on the sides of the container.

Observation under a polarizing microscope showed optical isotropy, confirming the fact that the crystal has cubic symmetry. A good cubic cleavage was found, but no cleavage was observed parallel to (111) or (110) planes.

Most of the X-ray data were obtained from Laue photographs and from photographs of line spectra from single faces. The apparatus used and the treatment of the spectral photographs were the same as those employed by Dickinson.<sup>3</sup> The angles and relative intensities of two reflections from the (111) face were measured on the X-ray spectrometer.<sup>4</sup>

### III. The Spectral Measurements and the Unit of Structure.

The values of the angles of reflection for different planes are given in the second column of Table I. The number of molecules per unit of structure and the dimensions of the unit were derived from these data. To

<sup>1</sup> Du Pont Fellow in Chemistry.

<sup>2</sup> P. Groth, "Chemische Krystallographie," Leipsic, 1906, vol. 1, p. 203.

<sup>3</sup> Dickinson, THIS JOURNAL, 44, 276 (1922).

<sup>4</sup> Dickinson and Goodhue, *ibid.*, 43, 2046 (1921).

find the number  $m$  of molecules in the unit of structure, the following well-known equation was employed.

$$\frac{n^3}{m} = \frac{8 \sin^3 \theta \cdot M}{\lambda^3 \rho N} \quad (1)$$

In this equation  $n$  denotes the order of reflection,  $\theta$  the angle of reflection from a (100) plane,  $M$  the molecular weight of the substance,  $\lambda$  the wavelength of the X-rays,  $\rho$  the density of the substance (1.52), and  $N$  the Avagadro number.

The length  $d_{100}$  of the unit cube, on the basis that  $m = 4$ , was calculated by the equation

$$n\lambda = \frac{2 d_{100} \sin \theta}{\sqrt{h^2 + k^2 + l^2}} \quad (2)$$

The values so calculated in  $10^{-8}$  centimeters are given in the sixth column of Table I.

TABLE I  
THE SPECTRAL MEASUREMENTS

Crystal Face	Angle of Reflection	Order of Reflection	Spectral Line	Wave-length	Length of Unit Cube	Intensity of Reflection
(100)	5° 23'	2	$Rh\alpha$	0.614	6.54	Strong
	10° 51'	4	$\alpha$	0.614	6.52	Medium
	16° 23'	6	$\alpha$	0.614	6.53	Weak
	4° 47'	2	$\beta$	0.545	6.54	
	4° 40'	2	$\gamma$	0.534	6.56	
(110)	7° 39'	2	$\alpha$	0.614	6.52	Strong
	15° 22'	4	$\alpha$	0.614	6.55	Weak
	6° 42'	2	$\beta$	0.545	6.60	
	6° 35'	2	$\gamma$	0.534	6.59	
(111)	5° 24'	1	Mo $\alpha$ } $\alpha$	0.710	6.53	100:153
	10° 51'	2				
(Mean)					6.55	

The value of  $d_{100}$  calculated directly from the density under the assumption that there are 4 molecules in the unit is  $6.55 \times 10^{-8}$  cm. This is equal to the mean of the above values. This value was used for calculations of the wavelengths from the Laue photographs.

#### IV. The Laue Photographs.

Laue photographs were taken with the beam of X-rays approximately perpendicular to the (100) face, and also with the beam approximately perpendicular to the (111) face. Gnomonic projections were made from the photographs, and the analysis carried out according to the method described by Wyckoff.<sup>5</sup> A gnomonic projection of an unsymmetrical photograph taken with the beam making an angle of 4° with the perpendicular to the (111) face, showing the 3-fold axis of symmetry, is repro-

<sup>5</sup> Wyckoff, *Am. J. Sci.*, 50, 318 (1920).

duced in Fig. 1. The area of each spot is proportional to the intensity estimated directly from the plate.

The smallest value of  $n\lambda$  for any plane, as calculated from Equation 2, was found to be  $0.24 \times 10^{-8}$  cm.; consequently it was deemed safe to consider any values of  $n\lambda$  between this value and  $0.48 \times 10^{-8}$  cm. to be pure first-order reflections. The forms giving reflections in the first order were: (311), (331), (531), (533), (551), (711), (731), (553), (731), (751), (753). Those appearing in the second order, but not in the first, were: (221), (320), (321).

All of the spots from planes reflecting in the first order on Laue photographs had comparative intensities such that the planes with the greater

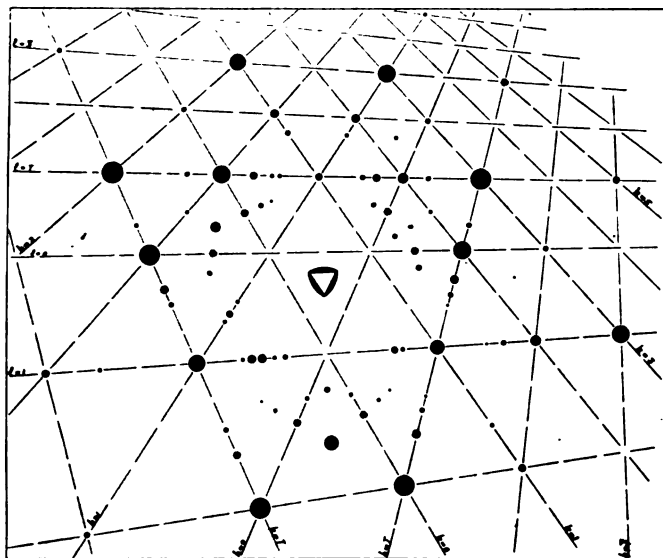


Fig. 1.

interplanar distance always had the greater intensity when reflecting with the same wavelength. Also, spots produced by second-order (221) planes could not be distinguished in intensity from those produced by first-order (531) planes; and second-order (321) reflections could not be distinguished in intensity from first order (731) reflections.

It was possible to obtain one additional piece of information from a powder photograph. From this it was clear that the second-order (100) reflection was more intense than the first-order (111) reflection.

## V. Interpretation of the Data.

The relative intensities of reflection of various orders shown in Table I are characteristic of crystals with the sodium chloride structure having

the halogen appreciably, but not too greatly, different in weight from the metal. Thus there is a rapid decline of intensity with increasing order for the planes (100) and (110), and a weaker reflection of the first order from (111) than of the second order. The facts shown by the powder photograph that the second order reflection from (100) was stronger than the first order from (111) in spite of the smaller value of  $d/n$  in the former case is also in agreement with a sodium chloride structure. In view of these facts and of the close resemblance between potassium cyanide and the alkali halides, the attempt has been made to satisfy the requirements of the remaining X-ray data on the assumption that the potassium atoms are located in the same way as the metal atoms in sodium chloride, and that the carbon and nitrogen atoms are near the corresponding halogen position. This assumption, whose approximate validity is clear from the above X-ray considerations, simplifies the treatment of the possible structures given below, which would otherwise contain three parameters to be determined.

Magnesium oxide is a crystal having the sodium chloride structure; and the application of the theory of space groups to this substance has been treated in detail by Wyckoff.<sup>6</sup> All the possible positions for the atoms of potassium cyanide are included in the possibilities given by Wyckoff for magnesium oxide. There are two possible arrangements for a substance having 4 molecules in the unit and 3 atoms in the molecule. These are,

- (a) K at : (u, u, u) (u,  $\bar{u}$ ,  $\bar{u}$ ) ( $\bar{u}$ , u,  $\bar{u}$ ) ( $\bar{u}$ ,  $\bar{u}$ , u)  
 C at : (v, v, v) (v,  $\bar{v}$ ,  $\bar{v}$ ) ( $\bar{v}$ , v,  $\bar{v}$ ) ( $\bar{v}$ ,  $\bar{v}$ , v)  
 N at : (w, w, w) (w,  $\bar{w}$ ,  $\bar{w}$ ) ( $\bar{w}$ , w,  $\bar{w}$ ) ( $\bar{w}$ ,  $\bar{w}$ , w)
- (b) K at : (u, u, u) ( $\frac{1}{2} + u, \frac{1}{2} - u, \bar{u}$ ) ( $\frac{1}{2} - u, \bar{u}, \frac{1}{2} + u$ ) ( $\bar{u}, \frac{1}{2} + u, \frac{1}{2} - u$ )  
 C at : (v, v, v) ( $\frac{1}{2} + v, \frac{1}{2} - v, \bar{v}$ ) ( $\frac{1}{2} - v, \bar{v}, \frac{1}{2} + v$ ) ( $\bar{v}, \frac{1}{2} + v, \frac{1}{2} - v$ )  
 N at : (w,  $\bar{w}$ , w) ( $\frac{1}{2} + w, \frac{1}{2} - w, \bar{w}$ ) ( $\frac{1}{2} - w, \bar{w}, \frac{1}{2} + w$ ) ( $\bar{w}, \frac{1}{2} + w, \frac{1}{2} - w$ ).

The arrangement (a) has tetrahedral symmetry, while (b) has tetartohedral symmetry. The first can be made to approximate the sodium chloride structure by giving u the value 0.25, and v and w values on either side of 0.75. The second can be made to approximate the sodium chloride structure by giving u the value zero and v and w values on either side of 0.50. Since the reflecting powers of carbon and nitrogen are probably about the same, these two arrangements are indistinguishable by the present methods of analysis, provided the atoms are in the positions indicated above. There is, moreover, a holohedral arrangement (Wyckoff's (j)), having 32 molecules in a unit (the  $d_{100}$  for which is  $13.10 \times 10^{-8}$  cm.), derivable from the space group  $O_h^5$ ; but this would also be indistinguishable from these. It suffices, therefore, to consider only the first arrangement.

For the intensity,  $I$ , of reflection of a given wavelength from any plane

<sup>6</sup> Wyckoff, *Am. J. Sci.*, 1, 138 (1921).

we may write:  $I = f(d/n) (A^2 + B^2)$ , where  $A$  is given by the following equation and  $B$  by a similar expression in sine terms.

$A = \bar{K}[\cos 2\pi n(h + k + l)u + \cos 2\pi n(-h + k - l)u + \cos 2\pi n(-h - k + l)u + \cos 2\pi n(h - k - l)u] + \bar{C}$  [a similar expression in  $v$ ] +  $\bar{N}$  [a similar expression in  $w$ ].  $\bar{K}$ ,  $\bar{C}$ , and  $\bar{N}$ , the reflecting powers of the atoms, were placed equal to the atomic numbers of potassium, carbon, and nitrogen, respectively;  $u$  was placed equal to 0.25, while  $v$  and  $w$  were independently varied by steps of 0.020 between 0.625 and 0.875. With these various values  $\sqrt{A^2 + B^2}$  was calculated for the planes for which data are available.

It was found on the Laue photographs that planes with all odd indices reflecting a given wavelength in the first order gave smaller intensities the smaller the value of  $d/n$ . Assuming that  $f(d/n)$  has smaller values the smaller  $d/n$  is, a satisfactory set of values of  $\sqrt{A^2 + B^2}$  should show no great variation, especially for planes having nearly equal values of  $d/n$ . It was also found that planes with any even index reflected in the second order with about the same intensity as planes with all odd indices in the first order when the values of  $d/n$  were the same. These planes with even indices should give about the same values of  $\sqrt{A^2 + B^2}$  as the other planes.

The best correspondence with the data seems to be obtained by placing  $v = 0.70$  and  $w = 0.80$ . The values of  $\sqrt{A^2 + B^2}$  calculated with these parameters, together with the values calculated for other parameters, are given in Table II for all of the planes whose calculated and observed intensities can be compared. Values of  $d/n$  in  $10^{-8}$  centimeters are given in Col. 3.

TABLE II  
CALCULATED VALUES OF  $\sqrt{A^2 + B^2}$

Order of Reflection	Plane	Value of $d/n$	Values of $\sqrt{A^2 + B^2}$ for		
			$u = 0.25$ $v = 0.70$ $w = 0.80$	$u = 0.25$ $v = 0.65$ $w = 0.85$	$u = 0.25$ $v = 0.75$ $w = 0.75$
1	(311)	1.97	48	86	24
1	(331)	1.50	59	72	24
1	(531)	1.11	76	63	24
2	(221)	1.09	80	87	128
1	(533)	0.99	76	82	24
1	(551)	0.92	76	34	24
1	(711)	0.92	104	65	24
2	(320)	0.91	71	116	128
2	(321)	0.88	72	86	128
1	(553)	0.85	76	94	24
1	(731)	0.85	93	71	24
1	(751)	0.76	76	61	24
1	(753)	0.72	76	82	24

It will be seen that the values of  $\sqrt{A^2 + B^2}$  calculated for  $u = 0.25$ ,  $v = 0.70$ ,  $w = 0.80$ , correspond satisfactorily with the observations. The only exception is that the calculated value for (711) is (104/76) or 1.4 times that calculated for (551), while the observed intensities of the (711) and (551) spots were the same as nearly as could be determined.

The intensities obtained from spectrometer measurements and from reflection photographs are in good agreement with the calculated values. The relative intensities of the spectra from a simple face can be estimated by assuming the normal decline to be 100:20:7. Values of the intensities so calculated are compared with the observations in Table III.

TABLE III  
CALCULATED AND OBSERVED INTENSITIES  
Relative Intensities Calculated for

Plane	$u = 0.25$ $v = 0.70$ $w = 0.80$	$u = 0.25$ $v = 0.65$ $w = 0.85$	$u = 0.25$ $v = 0.75$ $w = 0.75$	Observed Intensities
(100)	100:10:3	100:2:1	100:20:7	Rapid decline for the three orders
(110)	100:11	100:17	100:20	First order much stronger
(111)	100:218	100:51	100:570	100:153

## VI. Representation of the Crystal Structure.

Figure 2 represents  $1/8$  of the unit of structure, with the atoms placed in accordance with the values of the parameters,  $u = 0.25$ ,  $v = 0.70$ ,  $w = 0.80$ . The potassium atoms are represented by the larger circles, and the carbon and nitrogen atoms by the smaller ones. These latter atoms are equidistant from the corners of the cube not occupied by potassium atoms. Since the measurements do not serve to distinguish between the carbon and nitrogen atoms, both of these kinds of atoms are represented by the same sized circle. Table IV gives the distances

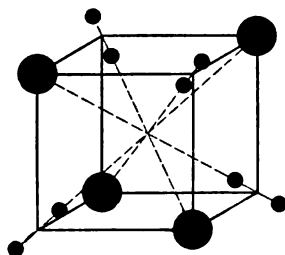


Fig. 2.

between the centers of the atoms, together with the sum of the corresponding Bragg radii,<sup>7</sup> both in  $10^{-8}$  centimeters.

TABLE IV  
DISTANCES BETWEEN THE ATOMS

	Distance	Sum of Bragg Radii
Carbon to nitrogen.....	1.15	1.4
Potassium to carbon.....	3.0	2.8
Potassium to nitrogen.....	3.0	2.7

<sup>7</sup> Bragg, *Phil. Mag.*, 40, 180 (1920).

Langmuir has suggested<sup>8</sup> that in the cyanide radical the carbon and nitrogen atoms possess in common an outer shell of electrons. If in accordance with this hypothesis the cyanide radical be regarded as a single atom for crystal structure purposes, potassium cyanide can be given the holohedral sodium chloride structure with four molecules in the unit; but if this be done, the values of  $\sqrt{A^2 + B^2}$  for (711) and (320) will, on the same assumptions used previously, be 24 and 128, respectively, and this would make the intensity of the (320) reflection  $(128/24)^2$  or 28 times as strong as that of the (711) reflection. This great discrepancy might be overcome by assuming the reflecting power of the cyanide radical to drop off much more rapidly than that of the potassium atom with decreasing values of  $d/n$ ; but there seems to be little present justification for such an assumption.

## VII. Summary.

The crystal structure of potassium cyanide has been studied with X-rays making use of the Laue photographic method, the spectrometric method, and the powder method. The X-ray data show conclusively that the structure of this substance approximates the sodium chloride structure. Consequently, the potassium atoms were placed at the sodium atom positions and the carbon and nitrogen atoms near the chlorine atom positions. The positions of carbon and nitrogen atoms which give the best agreement with the data place these atoms  $1.15 \times 10^{-8}$  cm. apart, equidistant from the position of the chlorine atom. The structure is represented in Fig. 2.

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## NOTES.

**Correlation of Atomic Structure and Spectra.**—In the July number of THIS JOURNAL there is a very interesting article by Bury<sup>1</sup> on a modification of the Lewis-Langmuir hypothesis of atomic structure. The sole change in this modification is that the fourth of Langmuir's postulates is altered to read as follows.

"The maximum number of electrons in each shell or layer is proportional to the area of its surface; thus, successive layers can contain 2, 8, 18 and 32 electrons. Groups of 8 and 18 electrons in a layer are stable even when that layer can contain a larger number of electrons. The maximum number of electrons in the outer layer of an atom is 8: more than 8 electrons can exist in a shell only when there is an accumulation of electrons in an outer layer. During the change of an inner layer from a stable group of 8 to one of 18, or from 18 to 32, there occurs a transition series of elements which can have more than one structure."

The only physical substantiation of this hypothesis which Bury stresses

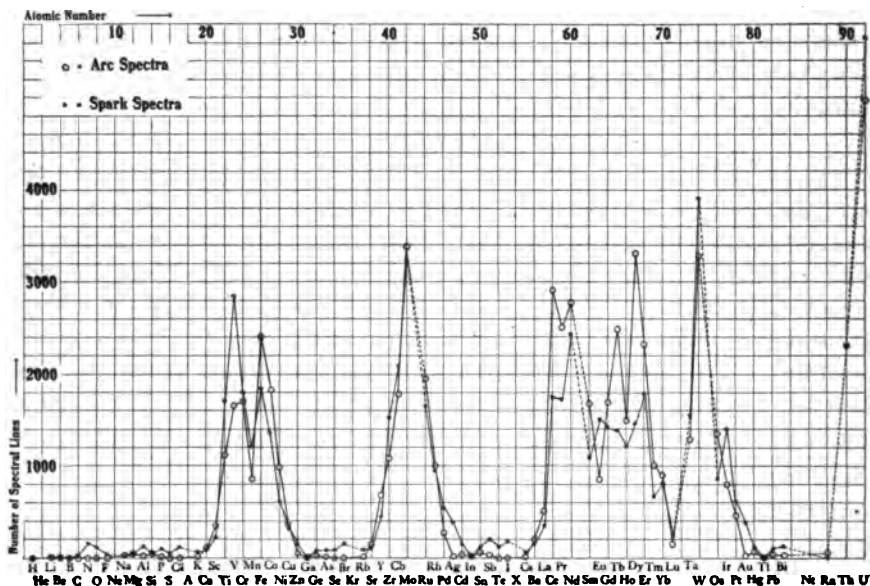
<sup>8</sup> Langmuir, THIS JOURNAL, 41, 905 (1919).

<sup>1</sup> C. R. Bury, *ibid.*, 43, 1602 (1921).



is the relation of atomic diameter of elements in a group of the periodic table with the number of electron shells in these elements. It seems that other data might also be employed which would test the plausibility of this hypothesis, namely, the data on the number of lines in the arc or spark spectra.

By plotting the atomic weights (or better the atomic numbers) as abscissas and the number of spectral lines as ordinates, Exner and Haschek<sup>2</sup> obtained periodic curves both for the spark and the arc spectra, the essentials of which are reproduced in Fig. 1. In the general form of the



curves, both are very similar and present the following main features. There are peaks between the elements Sc and Cu, Y and Pd, Ta and Pt. Th and U rise toward a peak at the end. There is also a plateau including most of the rare earths, that is, between Ce and Lu. The rest of the elements have relatively few lines.

Now, if it is assumed that it is only the electrons in the outer shell of the atom that are responsible for the spectral lines, then it may be supposed that in a general way, there is a relationship between the number of these electrons and the number of lines in the spectrum. Of course theoretically an infinite number of lines may be emitted by an element, but practically there are enormous differences between elements in this respect. By including only those lines given in Exner and Haschek's tables,<sup>3</sup> the rela-

<sup>2</sup> Exner and Haschek, "Die Spektren der Elemente bei Normalem Druck," Franz Deuticke; Leipzig, 1911, Vol. 1, p. 36.

<sup>3</sup> Exner and Haschek, Ref. 2, vols. 2 and 3.

tive numbers of lines in the spectra of the elements are placed on a more equable basis for comparison. If all lines except those between the wave lengths  $\lambda = 3,000$  and  $6,000 \text{ \AA}$ . were omitted, the comparative results would be essentially the same except that the plateau of the rare earths would be lowered due to their great richness of lines in the ultra-violet. A list of all the lines found either in the spark or in the arc spectra would be preferable to either alone. However, it is almost impossible to make such a compilation from Exner and Haschek's tables.

The number of lines in the arc and spark spectra of three groups of elements will be discussed herein with relation to the views of Bury and Langmuir on atomic structure,—namely (1) the elements of groups in the periodic table, (2) the transition elements and (3) the rare earth elements.

TABLE I

Element	Group	Arrangement of Electrons		Number of Line	
		Bury	Langmuir	Arc	Spark
Be	IIa	2.2	2.2	9	10
Mg	IIa	2.8.2	2.8.2	52	58
Ca	IIb	2.8.8.2	2.8.8.2	114	84
Zn	IIa	2.8.18.2	2.8.8.12	35	134
Sr	IIb	2.8.18.8.2	2.8.8.18.2	146	89
Cd	IIa	2.8.18.18.2	2.8.8.18.12	38	129
Ba	IIb	2.8.18.18.8.2	2.8.8.18.18.2	207	148
Hg	IIa	2.8.18.32.18.2	2.8.8.18.18.26	78	99
B	IIIa	2.3	2.3	2	3
Al	IIIa	2.8.3	2.8.3	28	115
Sc	IIIb	2.8.8.3	2.8.8.3	342	204
Ga	IIIa	2.8.18.3	2.8.8.13	14	14
Y	IIIb	2.8.18.8.3	2.8.8.18.3	684	430
In	IIIa	2.8.18.18.3	2.8.8.18.13	28	30
La	IIIb	2.8.18.18.8.3	2.8.8.18.18.3	512	356
Tl	IIIa	2.8.18.32.18.3	2.8.8.18.18.27	22	18

According to Bury, the elements of Group II of the periodic table all have two electrons in the outer shell, while Langmuir's hypothesis allows the members of the calcium series 2 electrons apiece but the beryllium series 2, 12 or 26. If the values for the number of lines given by Exner and Haschek are indeed comparable and if there is a qualitative relation between the number of such lines and the number of electrons in the outer shell, it will be seen in Table I that Bury's modification gives a better approximation to the facts observed by Exner and Haschek than the original hypothesis of Langmuir. Thus calcium and zinc according to Bury's arrangement of electrons should give approximately the same number of lines, while with Langmuir's arrangement, Zn would be expected to give six times as many as Ca. Considering that probably there is an increase of lines with increasing complexity of the core as shown by

the first three members of the group where both hypotheses agree, the number of lines given by alternating members of the group is remarkably uniform.

Group III of the periodic table is also included in Table I. It seems to be a general tendency for the *b* sub-group to give more lines than the *a* sub-group instead of the reverse as expected by Langmuir's hypothesis. In this connection it will be noted that in the *a* sub-group, after the first two members, there are 18 electrons in the outer shell of the core while in the *b* sub-group there are only 8 according to Bury. Naturally 3 electrons in the valence shell can arrange themselves more uniformly over 18 electrons than over 8. To substantiate this, Al, an *a* sub-group member with only 8 electrons in the second shell, has the largest number of lines of any member of its sub-group.

The transition elements, Bury suggests, have a variety of electron structures to account for their varying valences, an electron or electrons being pushed into an incompleated inner shell when the number of electrons in the outer shell becomes large. In Table II, the elements from K to Ge are arranged according to their atomic numbers. A transition group is included between these elements. Bury suggests that the number of varying structures increases roughly from Ti to Mn as a maximum and then decreases to Cu. If Bury's idea is correct, then each element having more than one form should give an entirely different spectrum for each

TABLE II

Element	Arrangement of Electrons Bury	No. of Lines	
		Langmuir	Arc Spark
K	2.8.8.1	2.8.8.1	18 61
Ca	2.8.8.2	2.8.8.2	114 84
Sc	2.8.8.3	2.8.8.3	342 204
Ti	2.8.8.4; 2.8. 9.3; 2.8.10.2	2.8.8.4	1123 1705
V	2.8.8.5; 2.8. 9.4; 2.8.10.3; 2.8.11.2	2.8.8.5	1642 2837
Cr	2.8.8.6; 2.8.11.3; 2.8.12.2	2.8.8.6	1697 1806
Mn	2.8.8.7; 2.8. 9.6; 2.8.11.4; 2.8.12.3; 2.8.13.2	2.8.8.7	865 1216
Fe	2.8.10.6; 2.8.12.4; 2.8.13.3; 2.8.14.2	2.8.8.8	2392 1838
Co	2.8.13.4; 2.8.14.3; 2.8.15.2	2.8.8.9	1830 1360
Ni	2.8.14.4; 2.8.15.3; 2.8.16.2	2.8.8.10	976 623
Cu	2.8.17.2; 2.8.18.1	2.8.8.11	368 328
Zn	2.8.18.2	2.8.8.12	35 134
Ga	2.8.18.3	2.8.8.13	14 14
Ge	2.8.18.4	2.8.8.14	27 62

different arrangement of electrons. These spectra superimposed on each other would result in a very complicated spectrum, rich in lines. This view predicts an increase in the number of lines to Mn and then a decrease. Moreover, there is a chance for lack of symmetry in the core of transition elements having the third shell containing between 8 and 18 electrons. These stable groups are probably symmetrically placed

in the shell, but this is not possible for such a structure as 2.8.13.3 for Fe. This irregularity would affect the positions of the valence electrons with consequent increase of the number of lines that may be produced. Langmuir's structure of the elements between K and Ge gives each element one more electron in the outer shell for each increase in atomic number. Thus it would be expected that the complexity of the spectra would increase all the way to Ge without a noticeable break. The number of lines does increase to Cr and Fe which are on either side of Mn which ought to be the true maximum, and then decreases steadily to Ga. This behavior accords with Bury's modification with the exception of Mn which is not vital.

There are similar peaks at the other transition groups. Thus between Y and Pd there is a very well defined peak with Mo at its maximum. The numbers of lines in the spectra of the elements of this transition group, *i. e.*, Y, Zr, Nb, Ru, Rh, and Pd fall almost exactly on the line drawn from Sr up to Mo and down to Ag. W forms the maximum of the peak of the third transition group and Th and U form the beginning of a fourth peak. Thus all the main peaks in Exner and Haschek's curves are accounted for by Bury's arrangement of electrons.

There remains only the plateau of the rare earth metals to be discussed. Langmuir's explanation of the structure of the elements of the rare earth metals shows the first member, La, with 3 electrons in the outer shell and then with each increase of one in the atomic number, an additional electron is added to the same shell. Lu thus is pictured with 17 electrons in the outer shell. The spectral curve should therefore become more and more complicated throughout the whole group without a drop at the end. It should blend into the third transition group without a break. Bury's explanation is that all the elements of this group may have a valence of 3, the excess electrons being added to an inner incompleated shell rather than to the outer shell. The first member and the last member of the group, La and Lu, have stable groups in the inner shells, but the intermediate elements have the fourth shell composed of from 19 to 31 electrons. It seems possible that there might be a choice of positions for the extra electrons in the inner shell which would give different kernels within the valence shell and thus cause such elements to be capable of producing a distinct set of lines for each arrangement. The non-symmetry of many of these structures would also tend to increase the number of lines. With the exception of La and Lu, the rare earth metals do give very complicated spectra with very large numbers of lines. The exceptions are interesting. La and Lu have stable systems in the inner shells and so would not be expected to give varying electron structures with consequent abundance of spectral lines.

Any relation of a property of the elements, such as the number of spectral lines, to the atomic number may lead to predictions concerning those elements as yet un-

known. There are six places vacant in the table of elements arranged according to atomic number, namely Nos. 43, 61, 72, 75, 85 and 87. Of these, No. 72 possibly is Urbain's celtium. But Bury's arrangement gives the electron structure 2.8.18.32.8.4 for this element which is consequently tetravalent, while Urbain describes celtium as being intermediate in chemical character between Lu and Sc, both trivalent elements. A further investigation of the chemical properties and the X-ray spectrum of celtium is therefore desirable.

Elements 43, 61 and 75 lie in approximately symmetrical positions on the curve of number of spectral lines plotted against atomic number. This relationship probably does not mean much in connection with No. 61, but may signify more in respect to Nos. 43 and 75. Thus they both would be expected to give very complicated spectra having large numbers of lines. Moreover, according to Bury, both would have similar electron structures, *i. e.*, 2.8.18.8.7 and 2.8.18.32.8.7. Since Bury thinks that in the second and third transition groups the electrons pass into an inner layer less readily than in that of the first long period, these elements Nos. 43 and 75 might be expected, if they really exist, to form compounds where they have high valences. Thus, in a search, one might look for them as cations rather than as anions.

### Summary.

It is shown that Bury's modification of Langmuir's hypothesis is at least consistent with the facts derived from a study of the number of lines in the arc and spark spectra of the elements as given in Exner and Haschek's tables.

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**Correction.**—Owing apparently to carelessness in proof-reading for which I am personally responsible, several very small errors exist in the tables of results in the paper by Baxter, Tani and Chapin<sup>1</sup> on the atomic weight of lanthanum. My attention has been called to this matter by Dr. Moles of the Laboratorio de Investigaciones Fisicas in Madrid. In order to avoid confusion the tables are reprinted below with the corrected figures starred. Fortunately, the changes do not affect the ultimate result in the least.

Ratio	At. Wt. La	Ratio	At. Wt. La
LaCl <sub>3</sub> : 3Ag		LaCl <sub>3</sub> : 3AgCl	
0.757888	138.912*	0.570543	138.969
0.757841	138.897	0.570394	138.905
0.757878	138.909	0.570391	138.904
0.757915	138.921	0.570331	138.878*
0.757930	138.925	0.570413*	138.913*
0.757917*	138.921*	0.570447*	138.927*
		0.570368	138.893
Av. 0.757895*	Av. 138.914*	Av. 0.570413*	Av. 138.913*

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<sup>1</sup> Baxter, Tani and Chapin, *THIS JOURNAL*, 43, 1804 (1921).

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF MCMASTER UNIVERSITY.]

## FRIEDEL AND CRAFTS' REACTION. DIPHENYL AND DITOLYL TETRAHALOGEN PHTHALIDES.

BY WALTER A. LAWRENCE AND HAROLD G. ODDY.

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This work was undertaken in order to study the diphenyl and ditolyl tetrahalogen phthalides, and to investigate the applicability of the method proposed by Rubidge and Qua<sup>1</sup> for the preparation of diphenyl-phthalide.

These authors heated phthalic anhydride, benzene and aluminum chloride together until hydrogen chloride was no longer evolved. An acid anhydride was then added and the heating continued for about 3 hours. The acid anhydride reacts with the intermediate compound formed and diphenyl phthalide is the final product. Of the acid anhydrides used, acetic anhydride was found to give the best results. This method was used in the experiments described below.

In the reactions described in this paper tetrabromo- and tetra-iodo-phthalic anhydrides were used with aluminum chloride and either benzene or toluene. In most cases good yields of the phthalides were obtained.

The diphenyl- and ditolyl-tetrachloro-phthalides have been prepared by Orndorff and Murray<sup>2</sup> who obtained them by treating tetrachloro-phthalyl chloride with benzene and toluene respectively. We prepared these two compounds by Rubidge's method and found them identical with Orndorff's products.<sup>3</sup>

**Tetrabromo-phthalic Anhydride with Aluminum Chloride and Benzene.**—Ten g. of anhydride was shaken up with 45 cc. of benzene and then 6.3 g. of aluminum chloride was slowly added. All the hydrogen chloride had been evolved after the mixture had stood for 9 hours on the water-bath at 80°. Seven cc. of acetic anhydride was added and the reaction was allowed to stand for 3 hours longer at the same temperature. Fifty cc. of 10% hydrochloric acid was then added and the excess of benzene was removed by distillation with steam; yield, 94%. The product was recrystallized from glacial acetic acid and melted at 202°. It is soluble in benzene, toluene and chloroform, slightly soluble in ethyl alcohol and insoluble in ligroin and water. This compound was found to be diphenyl-tetrabromo-phthalide.

*Analysis.* Calc.: Br, 53.16. Found: 53.5.

**Tetrabromo-phthalic Anhydride with Aluminum Chloride and Toluene.**—Ten g. of anhydride, 45 cc. of toluene, 6.3 g. of aluminum chloride and 7 cc. of acetic anhydride were used and the reaction carried out as above, except at 96–98°; yield, 93%. Recrystallized from glacial acetic acid, the product melted at 196–197°. It is soluble in benzene, toluene and chloroform, slightly soluble in ether and alcohol and insoluble in

<sup>1</sup> Rubidge and Qua, *THIS JOURNAL*, 36, 732 (1914).

<sup>2</sup> Orndorff and Murray, *ibid.*, 39, 294 (1917).

<sup>3</sup> The melting point of diphenyl-tetrachloro-phthalide is stated by Orndorff and Murray to be 250°; our product melted at 150°, and on second recrystallization at 151°. In a private communication Dr. Orndorff states that a typographical error occurred in their paper and that the melting point should have been given as 150°.

water. Method of preparation and analytical results show this substance to be ditolyl-tetrabromo-phthalide.

*Analysis.* Calc.: Br, 50.83. Found: 51.08.

**Tetra-iodo-phthalic Anhydride with Aluminum Chloride and Benzene.**—Ten g. of anhydride, 40 cc. of benzene, 4.4 g. of aluminum chloride and 6 cc. of acetic anhydride were taken, the temperature of reaction being about 80°. The phthalide obtained is soluble in benzene, toluene and chloroform, slightly soluble in ether, ligroin and ethyl alcohol, and insoluble in water. When recrystallized from glacial acetic acid it melted at 206°; yield, 61%. It has a very pale yellow color. This compound was shown to be diphenyl-tetra-iodo-phthalide.

*Analysis.* Calc.: I, 64.33. Found: 64.01.

**Tetra-iodo-phthalic Anhydride with Aluminum Chloride and Toluene.**—The reaction was carried out as above at 97–98° with 10 g. of anhydride, 40 cc. of toluene, 4.4 g. of aluminum chloride, and 6 cc. of acetic anhydride. The product was treated with small quantities of cold acetone to remove the tar formed during the reaction. The residue was recrystallized from glacial acetic acid and melted at 213–214°; yield, 42%. It is soluble in benzene and chloroform, and slightly soluble in ethyl and methyl alcohols ether and ligroin. Our purest product had a pale yellow color. The synthesis and analysis show this substance to be ditolyl-tetra-iodo-phthalide.

*Analysis.* Calc.: I, 62.1. Found: 62.5.

### Summary.

1. The method used by Rubidge and Qua for the preparation of diphenyl phthalide was found to give good results in the preparation of the diphenyl and ditolyl tetrahalogen phthalides.

2. Four new substituted phthalides have been prepared and their properties described: diphenyl-tetrabromo-phthalide, m. p. 202°; ditolyl-tetrabromo-phthalide, m. p. 196–197°; diphenyl-tetra-iodo-phthalide, m. p. 206°; ditolyl-tetra-iodo-phthalide, m. p. 213–214°.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA.]

## THE REARRANGEMENT OF BENZIL TO BENZILIC ACID.

BY ARTHUR LACHMAN.

Received August 29, 1921.

The mechanism whereby benzil, under the influence of alkalis, is converted into benzilic acid has long been a matter of speculation. Four different hypotheses have occupied the attention of recent investigators. Nef<sup>1</sup> assumed an addition of water to benzil, followed by dissociation into benzophenone and "dioxymethylene;" the latter substance, after changing over into formic acid, was then supposed to condense with the former by carbonyl condensation, thus yielding benzilic acid. Schroeter<sup>2</sup> postulated the intermediate formation of diphenylketene. This view, however, has been tested experimentally by Nicolet and Pelc,<sup>3</sup> and found untenable. Tiffeneau, recognizing the analogy between the benzil rearrangement

<sup>1</sup> Nef, *Ann.*, 298, 372 (1897).

<sup>2</sup> Schroeter, *Ber.*, 42, 2336 (1909).

<sup>3</sup> Nicolet and Pelc, *THIS JOURNAL*, 43, 935 (1921).

and that of pinacol into pinacolone, has adapted his theory of the latter process<sup>4</sup> to the somewhat different conditions applying in the case of benzil. Michael,<sup>5</sup> in a purely critical consideration of these explanations has found them all unsatisfactory; according to him, the rearrangement of benzil is caused by "the great positive energy of the alkali" employed as reagent.

An experimental study of this puzzling behavior of benzil has brought facts to light which definitely rule out the hypotheses of Nef, Tiffeneau and Michael. This work was suggested by the recently completed investigation of dihydroxy-tartaric acid<sup>6</sup> during which the striking resemblance of this acid to benzil was noted. Dihydroxy-tartaric acid, warmed with alkali, rearranges to give tartronic acid; this process is quite analogous to the benzil transformation. Dihydroxy-tartaric acid, whose carboxyl groups hold water and are therefore  $C(OH)_2$  groups, is able to undergo rearrangement simply through the action of heat.<sup>7</sup> Is it not possible that benzil, given sufficient time and temperature increase, might add water and produce benzilic acid?

### The Action of Water on Benzil.

Michael and Tiffeneau base their theoretical views on the preliminary addition of alkali to the benzil molecule. It is strange that they both overlooked the significance of an observation recorded many years ago by Klinger.<sup>8</sup> Klinger exposed a solution of benzil in moist ether to the action of sunlight; among the reaction products he found benzilic acid.

It was therefore extremely probable that water alone would convert benzil into benzilic acid. The first attempts, however, were not very encouraging. Varying amounts of the two materials were heated in sealed tubes for periods up to 10 hours and to temperatures up to 235°. In all cases, mere traces of benzilic acid were formed, and the benzil was recovered practically completely and with unchanged melting point.<sup>9</sup>

<sup>4</sup> Tiffeneau, *Rev. gen. sci.*, 18, 584 (1907).

<sup>5</sup> Michael, *THIS JOURNAL*, 42, 812 (1920).

<sup>6</sup> Lachman, *ibid.*, 43, 2091 (1921).

<sup>7</sup> Solutions of the free acid (and its salts) change into tartronic acid even at room temperature; the process is completed within a few days.

<sup>8</sup> Klinger, *Ber.*, 19, 1868 (1886). No quantitative data are given; the period of exposure was 4 months. The observation is correct. By means of the colorimetric method described below, it is very easy to follow the progress of this conversion. The ethereal solution is extracted at intervals with small amounts of sodium carbonate solution. Ten g. of benzil, dissolved in 100 cc. of moist ether, gave no test for benzilic acid after 3 days. After 15 days, 0.0015 g. was noted; after 35 days, 0.0020 g. additional was found. The study of this photochemical reaction is being continued.

<sup>9</sup> Minute amounts of benzilic acid may be estimated with fair accuracy by means of the intense purple color which the substance gives with conc. sulfuric acid. Standards may be made with from 0.0005 to 0.0050 g. dissolved in a few drops of water or alcohol



When the mode of procedure was changed, and benzil was heated under a reflux condenser with large quantities of water, for much longer periods (up to 120 hours), much larger amounts of benzilic acid were obtained. The solubility of benzil in boiling water was found to be 0.33 g. per liter. The solution has a decided yellow color; when it cools, it deposits very slender, and very pale needles. These melt at the same temperature as the original material.

The isolation of benzilic acid from the reaction mixtures was effected as follows. After cooling the material to room temperature, it was made alkaline by the addition of a few cubic centimeters of sodium carbonate solution, and then extracted twice with ether. The alkaline solution was evaporated to about 15 cc., cooled, acidified with hydrochloric acid in slight excess, and extracted with ether. The ether extract was dried at 100° and weighed. Its melting point was then taken. Control tests, each of 1 liter of cold saturated aqueous solution of benzil, gave no benzilic acid whatever when subjected to the process just described.

The first series of measurements gave the following data.

Time Days	Water Cc.	Benzil G.	Benzilic Acid G.	M. p. ° C.
3	1000	10	0.04	140
3	1000	10	0.07	142
5	750	1	0.06	145
3	750	1	0.05	143

The melting points indicate a relatively high degree of purity in the product, and in particular the absence of any considerable proportion of benzoic acid. Pure benzilic acid melts at 149–150°; a mixture with 5% of benzoic acid melts at 142–143°; with 10%, at 134–135°.

These results showed that the active mass, in the conversion of benzil to benzilic acid, is solely the dissolved portion, *i. e.*, 0.33 g. per liter. Based on this amount, the yields of benzilic acid obtained are relatively large.

The method by which these figures were obtained did not lend itself to accurate measurement; but as the data showed that practically no other acid product than benzilic acid was formed, a series of observations was made in which the final acidity was determined. Three flasks containing benzil and water were sealed and kept for 5 days in an electrically heated air-bath. The temperature ranged between 95° and 100°.

The water had previously been boiled to remove carbon dioxide; the and made up to 25 cc. with pure sulfuric acid. If protected from atmospheric moisture these solutions will keep for days. Benzil and benzophenone do not interfere. Benzohydrol gives a brick-red color, but much less intense; it may be removed by ether extraction after rendering the sample alkaline. Phenolphthalein interferes with the benzilic test, and should be employed only as an outside indicator.

flasks were of Pyrex glass, and had been steamed out. At the end of the heating period the flasks were cooled to room temperature, the contents filtered cold, and promptly titrated cold with 0.1 *N* sodium hydroxide solution, with phenolphthalein as an indicator. The following data were secured.

Benzil G.	Water Cc.	NaOH Cc.	Equivalent benzilic acid G.
1.523	500	0.80	0.018
0.884	500	0.65	0.015
0.461	500	0.75	0.017

These figures are somewhat lower than the previous set, despite the longer time period. The temperature was a little lower, however; and the first series may have been slightly influenced by alkali from the glass. Such an influence is excluded here: *free acid only* is recorded.

#### Action of Very Weak Alkali on Benzil.

Michael's discussion of the benzil rearrangement begins with this statement:<sup>10</sup> "There is no indication of the formation of a hydrated benzil but, even accepting its existence during the reaction, it is certain that alkali would rupture the carbon linkage and form sodium benzoate and benzaldehyde, etc." It has just been shown that water by itself produces little or no benzoic acid. The effect of small amounts of alkali was therefore investigated.

One g. of benzil was boiled with 750 cc. of water as before, with the addition of 5.0 cc. of *N* sodium hydroxide solution. If all the benzil were converted into either benzilic or benzoic acid, 4.4 cc. would be used up. The normality of the alkaline solution at the start was 0.0066. Boiling was continued for 2 days when it was found that 2.5 g. of sodium hydroxide was used up, and 0.55 g. of benzilic acid obtained of m. p. 142°. A duplicate was refluxed for 3 days; 2.8 g. of sodium hydroxide was used up and 0.61 g. of benzilic acid (m. p. 139°) obtained.

The melting points are depressed in part by the phenolphthalein present, and perhaps by other impurities as well: in fact, the crude benzilic acid darkened considerably as it dried before it was weighed, and blackened when it melted; whereas mixtures of pure benzilic and benzoic acids may be re-melted several times without change of color, if not overheated. It is clear, therefore, that the amount of benzoic acid formed during the action of very weak alkali on benzil must be even less than the melting points would indicate, and that 5% is an upper limit.

The action of weak alkali on benzil is seen to differ from that of pure water only in the rate at which the rearrangement takes place. The catalytic effect of the alkali, in the concentration employed, is quite moderate; the rate being increased about 20 times. Inasmuch as the hydroxyl-

<sup>10</sup> Ref. 5, p. 812.

ion concentration in the alkali is nearly 10,000 times greater than in the water, the hydroxylion as such is not an essential factor in the transformation. The relative unimportance of this ion is shown also by the final acid reaction when water alone is the reagent.

The views of Tiffeneau and of Michael are inadequate to explain the data just recorded, and they fail to account for the photochemical observations of Klinger.

The conversion of benzil into benzilic acid, therefore, is accurately represented by the equation,



This equation, however, is purely qualitative; for it is obvious from the experimental results that the reaction does not reach completion, and that some as yet unrecognized factor is impeding it.

### Is the Benzil Rearrangement Reversible?

The heats of combustion of benzil and of benzilic acid are almost identical (1625 and 1619 Cal. respectively). The change in free energy during the rearrangement must therefore have a very low value, and from this point of view the reversal of Equation 1 does not appear at all improbable. Such a reversal would have considerable significance. For this reason, the conflicting data thus far obtained are given here, in the hope that they may eventually lead to a solution of this problem.

Three g. of imported benzilic acid was refluxed with 1 liter of water for 2 days. After the solution had been rendered alkaline, ether extraction gave 0.08 g. of benzil, m. p. 90°. But another sample of the same lot, not previously refluxed with water, was found to contain 0.06 g. of benzil. Therefore, a portion of this benzilic acid was carefully purified. It was first dissolved in a slight excess of potassium carbonate solution, and this solution was extracted with ether. The alkaline solution was evaporated, and the crystals of potassium benzilate were recrystallized. This purified salt was then precipitated fractionally (1) with dil. acetic acid, (2) with conc. acetic acid, (3) with hydrochloric acid. All 3 fractions melted sharply at 149.5°. This material was used for all further experiments.

As it was possible that the imported material was originally pure, but had slowly reverted (it was at least 8 years old), a weighed portion of the purified product was heated in a sealed tube to 100° for 10 days. Its acidity was then found to be unchanged, so that no benzil could have been formed under these conditions.

Three separate portions of 1.0 g. each were refluxed with water for 3 days. Ether extraction of two of these gave mere traces of oil; in the third case, 0.03 g. of benzil melting at 87° was obtained, which after recrystallization melted at 92°. In this instance, the yellow crystals of benzil were noted in the reflux condenser on the second day.

This result has not been obtained again. Two further trials, with longer boiling, gave small yields of benzophenone, with no visible content of benzil. The benzophenone was converted into its oxime, which melted sharply at 140°, and could have contained but little impurity. Furthermore, no benzil was observed when benzilic acid was

boiled in the presence of an equivalent amount of hydrochloric acid; the same was true when the benzilic acid was partly or almost wholly neutralized.

Thus, the behavior of benzilic acid is seen to be erratic, and subject to influences which have so far escaped observation. This is clearly shown in the following series of data.

### The Change from Benzilic Acid to Benzophenone.

A large volume of a nearly saturated solution of benzilic acid was prepared. Five hundred cc. of this required 36.2 cc. of 0.1 *N* alkali for neutralization at the boiling point, with phenolphthalein as an indicator, and 36.1 cc. at room temperature. Both solution and alkali were therefore free from carbon dioxide within the limit of experimental error. Benzilic acid in this concentration is not appreciably volatile with steam; 500 cc. was boiled briskly for 15 minutes, and then titrated; 36.0 cc. of alkali was needed. The normality of this stock solution was 0.00724, equivalent to 1.650 g. of benzilic acid per liter.

Seven portions of 500 cc. each were sealed in Pyrex flasks, and heated at 105° for the periods of time shown below. Flasks 3 to 7 were heated simultaneously. After cooling to room temperature, the flask contents were titrated directly. Very uneven results were obtained.

Flask	Time Days	NaOH Cc.	Total %	Acidity lost per day %
1	2	34.8	3.9	1.9
2	2	35.2	2.8	1.4
3	3	34.7	4.3	1.4
4	5	31.9	11.9	2.4
5	5	34.8	3.9	0.8
6	5	31.7	12.5	2.5
7	5	34.6	4.4	0.9

The contents of Flasks 1 and 2 were combined after neutralization, and extracted carefully with ether. This gave an oily residue, weighing when dry 0.045 g.; calc. for benzophenone, 0.044 g. The contents of Flasks 4 and 6 were cloudy when cool. From 4 there was obtained 0.069 g. of oxime melting at 140° (calc., 0.085 g.), a recovery of 81%. The contents of Flasks 5, 6 and 7 combined gave 0.15 g. of oxime, melting at 138° (calc. 0.14 g.).

In several instances, during this work on benzilic acid, the ether extracts gave a strong color reaction for benzohydrol with sulfuric acid, but no benzohydrol was actually isolated at any time. A control test, to see whether by chance benzohydrol could form benzophenone oxime with hydroxylamine, was negative.

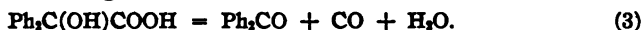
When exposed to sunlight for 15 days, 500 cc. of the same benzilic acid solution used only 27.5 cc. of sodium hydroxide solution, a loss of 22%. The oxime melted at 118° and carried an oily admixture; after recrystallization, it melted at 139°.

The above data, despite the irregularity observed as to rate, clearly show that the formation of benzophenone is proportional to the loss in acidity which is suffered by the benzilic acid. The reaction therefore cannot be represented by



(2)

Klinger and Standke,<sup>11</sup> who have studied the decomposition of benzoic acid by prolonged heating to 180°, found that the chief reaction is



This equation also represents the behavior of the acid when it is boiled with water.<sup>12</sup>

There is no likelihood that formic acid is first formed according to Equation 2, and that it immediately breaks down *completely* into water and carbon monoxide. Dr. Branch has been kind enough to calculate that at least 10 times as much formic acid as could be produced in the above experiments would be in stable equilibrium with water and carbon monoxide.<sup>13</sup>

These data leave no room for Nef's hypothesis that benzil is converted into benzoic acid *via* benzophenone and "dioxymethylene." The series of events is, Benzil  $\rightarrow$  Benzoic acid  $\rightarrow$  Benzophenone, and not Benzil  $\rightarrow$  Benzophenone  $\rightarrow$  Benzoic acid.

### The Mechanism of Rearrangement.

No one of the four "explanations" of the benzil rearrangement that have received serious attention is capable of accounting for the facts recorded above. During the course of this experimental study, a working hypothesis has been developed which has the practical merit of grouping many diverse processes under a single point of view, and of suggesting new modes of approach such as have just been described. Previous investigators have devoted their attention chiefly to abnormal readjustments in the carbon chain—abnormal because infrequent and contrary to the teachings of structural theories—and have overlooked the features which these rearrangements have in common with other reactions, in which no alteration of the carbon chain is involved.

The benzil conversion, like that of pinacol, and like that of dihydroxy-tartaric acid, is not only a rearrangement, but also an intramolecular oxidation-reduction process.<sup>14</sup> If we permit ourselves to make one single assumption, all of these diverse reactions and with them many others, find a simple explanation.

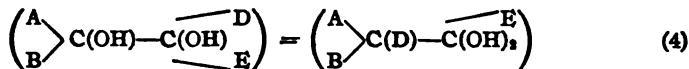
<sup>11</sup> Klinger and Standke, *Ber.*, 22, 1213 (1889).

<sup>12</sup> The amount of carbon monoxide formed is so small, under the conditions of the above experiments, that extremely careful gasometric methods would be required to show accurate proportionality. 500 cc. of benzoic acid solution was boiled as before, after pumping out air as much as possible. After 5 days, during which time the apparatus was sealed, the gases were pumped out again. 8.3 cc. was obtained, of which 6.7 cc. was absorbed by cuprous chloride. The benzoic acid solution had lost acidity equivalent to 2.7 cc. of 0.1 *N* sodium hydroxide solution.

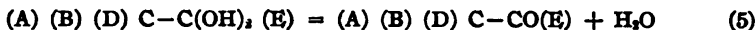
<sup>13</sup> Branch, *THIS JOURNAL*, 37, 2316 (1915).

<sup>14</sup> Michael has indeed attempted to bring both rearrangement and intramolecular oxidation under one point of view; but his assumptions as to the rôle played by reagents and solvents are out of harmony with the facts recorded above.

This assumption is that hydroxyl groups attached to adjacent carbon atoms tend to unite with *one* of these carbon atoms and, in so doing, the mobile hydroxyl group exchanges places with some other atom or radical. The typical equation of this process is,



followed by loss of water,



The assumption of a mobile hydroxyl group is not new. Lieben<sup>15</sup> was among the first to suggest it for the pinacol rearrangement. There seems, however, to have existed a strong prejudice against the assumption of mobility for anything except hydrogen. Michael, in his recent critique, did not mention Lieben's hypothesis. Tiffeneau dismissed it somewhat satirically.<sup>16</sup> Meerwein,<sup>17</sup> whose recent work has brought out evidence strongly corroborative of the views here set forth, gave it some thought, but could not find in it a sufficient degree of "Notwendigkeit," and therefore adopted the views of Tiffeneau; but he expressed his conviction that the pinacol rearrangement was an "immediate" process, without any intermediates whatever.

It is clear that under favorable conditions, rearrangements involving merely an exchange of hydroxyl with some other group, might be expected to occur by heating a substance without any reagents whatever, for a long enough period and to a sufficiently high temperature. In the case of sodium dihydroxy-tartrate, a few days at room temperature suffice, as does a single hour at 150°. The behavior of hydrated benzil has just been described. The pinacols rearrange under the influence of heat alone.<sup>18</sup> The transformation of tartaric acid into pyruvic acid has been explained by Chattaway and Ray<sup>19</sup> as an exchange of hydrogen and hydroxyl; this is a typical intramolecular oxidation-reduction reaction, and is induced by moderate temperature increase.

It is not possible, with our present knowledge, to form any definite conception of the *driving force* in these intramolecular processes. In the case of the pinacols, rearrangement is greatly facilitated by dehydrating agents; and it might have seemed as if the free energy of the formation

<sup>15</sup> Lieben, *Monatsh.*, 23, 63 (1902).

<sup>16</sup> Tiffeneau's phrase is "une sorte de chassé-croisé."

<sup>17</sup> Meerwein, *Ann.*, 396, 209 (1913); 419, 121 (1919).

<sup>18</sup> This statement regarding the pinacols is at variance with the published reports of Thorner and Zincke. Professor T. D. Stewart is now investigating the question experimentally.

<sup>19</sup> Chattaway and Ray, *J. Chem. Soc.*, 119, 34 (1921). They were investigating the well-known dry distillation of tartaric acid. I have since found that *solutions* of tartaric acid in water yield pyruvic acid and carbon dioxide steadily on prolonged boiling.

of water were the sufficient as well as the necessary factor. But Vorländer<sup>20</sup> has shown that dilute solutions of weak organic acids, which can hardly be classed as dehydrating media, will bring about pinacolone formation; and it has been shown, that the benzil rearrangement takes place with the *addition* of water. We must therefore distinguish between *water formation* as a causating factor, as in ester synthesis, and *water separation* as an incident, as in the pinacols.

The most striking feature of these rearrangements, from the standpoint of affinity problems as well as of atomic structures, is that perfectly symmetrical compounds, such as pinacol, benzil, tartaric acid, dihydroxytartaric acid and oxalic acid, represent, in fact, unstable equilibria. When we come to know why such structures are unstable, we shall know what is the cause of rearrangement. Meanwhile, we must be satisfied with the somewhat awkward phrase "intramolecular oxidation and reduction."<sup>21</sup>

Rearrangements of carbon chains, as viewed here, are merely a special case of a general phenomenon. If, in Equation 4, one of the groups A, B, D, E, is hydrogen, that will usually be the one to exchange places with hydroxyl. If no hydrogen is so present, a radical such as methyl, phenyl or carboxyl will shift to take the place of the mobile hydroxyl.

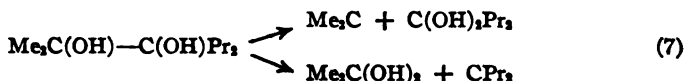
If the compound (COH)<sub>2</sub>ABDE is symmetrical, only one "metaklinic" product can result; but if it is unsymmetrical, two or more may be expected. Meerwein's latest work has proved this in convincing fashion, setting a standard of experimental completeness worthy of emulation.

The following convention is suggested for the formulation of such shifts, using the pinacol rearrangement as an example.



The division sign is used to indicate that an hydroxyl group has moved (in this case to the right) and that the vacant bond will be occupied by a shift from that side.

Meerwein has found that in dimethyl-dipropyl glycol the shift occurs in two directions; and, as might be expected from the close resemblance between methyl and propyl, in nearly equal proportions.



Similar results were found by him in the case of dimethyl-dibutyl glycol.<sup>22</sup>

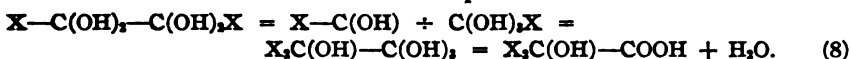
<sup>20</sup> Vorländer, *Ber.*, 30, 2266 (1897). For a discussion of this phase of the rearrangement problem, cf. Michael, *Ref.* 5, p. 802.

<sup>21</sup> A short word may prove desirable. The verb *metaklinomai* (Gr.) (to shift cargo from one side to another) offers an apt analogy. We may speak of *metakliny* or of the *metaklinic* process.

<sup>22</sup> The observed proportion of methyl shift to propyl shift is 10:8; of methyl to butyl, 7:4. Meerwein is studying the factors that determine preference in shifting. Tiffeneau, who has done valuable work in this same field, found that in most cases

Experimental studies in the field of rearrangement are greatly complicated by the occurrence of side reactions. These may be of the most diverse sort; chief among them is a tendency to rupture the bond connecting the carbon atoms to which the hydroxyl groups are originally attached. This rupturing process may at times become the main reaction, with rearrangement greatly subordinated; such seems to be the case with the aromatic pinacols.<sup>22</sup>

Coming now to the consideration of the benzil rearrangement, we may for the present assume that each of the carbonyl groups is capable of adding water, in analogy with dihydroxy-tartaric acid. Using X to represent either phenyl or carboxyl, we may use a single set of equations for the behavior of both of these compounds.



It is an advantage of this method of formulation that it indicates the nature of the rupture products as well. Benzil is ruptured to give benzoic acid and benzaldehyde; dihydroxy-tartaric acid yields oxalic and glyoxalic acids.

The decomposition of benzilic acid described above may be accounted for in similar fashion, as a combination of shift and rupture.



It would require far too much space to point out the wide applicability of the reactions typified by Equations 6, 8, and 9. A very few illustrations will suffice. The formation of acrolein on heating glycerine is an exchange of hydrogen and hydroxyl. The interconversion of glucose, mannose and fructose is an addition of water to the carboxyl group, followed by exchange of hydrogen and hydroxyl. The formation of methylglyoxal from glucose may be accounted for by the shift of 2 hydroxyl groups, followed by rupture. The conversion of methylglycol into a mixture of acetone and propionic aldehyde is a shift of hydroxyl in 2 directions, quite similar to Meerwein's results in the more complicated glycols. The breakdown of benzoyl-formic acid into carbon monoxide and benzoic acid, and of oxalic acid into carbon monoxide and carbonic acid, are analogous to the decomposition of benzilic acid.

phenyl is more labile than methyl. Tiffeneau, however, has not been consistent in developing the quantitative side of this phenomenon. It may be possible some day to establish a "*metaklinic*" series indicating the relative ease of shift of the various radicals. Hantzsch has done something like this in the case of the Beckmann rearrangement.

<sup>22</sup> Benzyl ether (Cannizzaro, *Ann.*, 92, 113 (1854); Lowe, *ibid.*, 241, 374 (1887)), on heating, breaks down into benzaldehyde and toluene:  $\text{Ph}-\text{CH}_2-\text{O}-\text{CH}_2-\text{Ph} = \text{PhCHO} + \text{PhCH}_3$ . This reaction is now being investigated; it seems to offer an opportunity for the quantitative study of "*metaklinic*," free from the complications caused by side reactions.



### Conclusion.

The electronic conception of intramolecular oxidation and reduction accounts for the phenomena just described, by stating that the oxidized carbon atom loses, and the reduced carbon atom gains, an electron. From this point of view, electron movement and hydroxyl movement are reciprocal; and it may well be that they stand to each other in the relation of cause and effect.

It is difficult, however, to derive any helpful suggestions from this source, in the present state of our information; and it seems more useful to adhere to the established customs of structural interpretation. When we know more about the behavior of the electrons of carbon, there will be no difficulty in re-interpreting the facts of rearrangement.

Meanwhile, we can state only as experimental facts, the comprehension of which escapes us, that if two (or possibly more than two) carbon atoms in a compound are in a symmetrical or in a similar state of oxidation, such a structure is unstable; that one of these carbon atoms tends to a greater degree of oxidation, the other becoming reduced; that this tendency is enhanced by an increase of temperature, and may be greatly accelerated by a variety of catalysts; and that the forces concerned in or released by it are powerful enough, at times, to overcome the forces that bind carbon atoms together.

I must acknowledge my heavy indebtedness to Professors Stewart, Porter and Branch, of California, and to Professor Stieglitz, of Chicago, for their helpful suggestions and still more helpful criticism during the preparation of this paper.

### Summary.

1. Benzil is converted into benzilic acid by boiling with water.
2. The action of very weak alkali differs from that of water only by being somewhat faster, but by no means in proportion to the increase in hydroxyl ions.
3. The reversal of the benzil rearrangement is not unlikely, but has not yet been accomplished.
4. Benzilic acid, on boiling with water, yields benzophenone and carbon monoxide.
5. The previous theories of rearrangement do not account for the observed facts.
6. A theory of rearrangement is offered, based upon the forces concerned with intramolecular oxidation and reduction.
7. This theory brings a wide variety of facts into relation with one another.

BERKELEY, CALIFORNIA.

[CONTRIBUTION FROM THE DIVISION OF AGRICULTURAL BIOCHEMISTRY, UNIVERSITY OF MINNESOTA.]

## SULFUR IN PROTEINS. I. THE EFFECT OF ACID HYDROLYSIS UPON CYSTINE.<sup>1</sup>

BY WALTER FRED HOFFMAN AND ROSS AIKEN GORTNER.<sup>2</sup>

Received August 30, 1921.

### Introduction.

The protein molecule has been the subject of many investigations, and a very voluminous literature has resulted. In spite of the enormous amount of work which has been done in this field there are still many problems which remain to be solved. One of these is the question as to whether or not the peptide linkage is the only important grouping joining the individual amino acids. Theoretically there is a possibility of a number of other linkages in which reactive groups other than amino or carboxyl are involved. There is a possibility that ethers or esters are present. The  $\alpha$  hydrogen on the indole nucleus is so reactive that it appears almost inconceivable that it does not sometimes become involved in the reactions within the protein molecule. However, none of these modes of union has been demonstrated in protein material. The only form of linkage, aside from the peptide group, which has been demonstrated is the  $-S-S-$  linkage in cystine. From a study of the literature it appears that this is the principal form in which sulfur occurs in the protein molecule. The reduced amino acid cystein,  $SH-CH_2-CH(NH_2)COOH$ , of which cystine is the disulfide, has never been proved to be present, as such, in protein material. Certain physico-chemical data, however, argue for its presence. For example, casein contains about 0.80% of sulfur. On the theory that this sulfur represents one molecule of cystine there must be present two atoms of sulfur with a resulting molecular weight of 8015 for the casein molecule. We have, however, good physico-chemical evidence that the molecular weight of para-casein is approximately 4000, in which case only a single atom of sulfur can be present in the para-casein molecule. Cystine has been isolated from the tryptic digest of casein, but in view of the readiness with which cystein can be oxidized to cystine the presence of cystine instead of cystein in the casein molecule still remains an open question.

In view of the uncertain knowledge regarding the sulfur linkages in protein it appeared wise to plan an extensive investigation in this field. The present paper is the first of a series of papers. Experimental work on subsequent papers is already well advanced.

<sup>1</sup> Published with the approval of the Director as Paper No. 273, Journal Series, Minnesota Agricultural Experiment Station. Presented before the Organic Division of the American Chemical Society at the New York Meeting, September, 1921.

<sup>2</sup> Dr. George E. Holm, formerly of this Division, assisted in the plan of the experimental work.

### Historical.

The Behavior of Cystine and Cystine Sulfur Towards Chemical Reagents and the Relation of Cystine to the Sulfur Content of Proteins.—Fleitmann<sup>8</sup> was the first to show that the sulfur in proteins may not all be in one compound or composition. He found that only a part of the sulfur was removed from certain proteins when heated with alkali. On account of their peculiar behavior and their similarity to cystine and taurine, the sulfur compounds then known to be related to animal metabolism, he called the two forms, *oxidized* and *unoxidized* sulfur. Danielewski<sup>9</sup> confirmed Fleitmann's observations and later<sup>1</sup> called attention to the fact that this peculiar property of sulfur in proteins had been neglected by those trying to establish formulas for proteins, as most of these were made on the basis of one sulfur atom. Krüger<sup>6</sup> was the first to produce evidence that the terms "oxidized" and "unoxidized" sulfur were not correct. He carefully determined the amounts of the two forms of sulfur in ovalbumin and fibrin and showed that mercaptans and thio-ethers behave in a similar manner when heated with alkali. But he also observed that oxidized sulfur compounds as sulfonic and sulfinic acids behave quite differently and were decomposed under the same treatment giving alkali sulfites. For this reason he dropped the terms oxidized and unoxidized sulfur and named the two forms *loosely* and *firmly bound* sulfur. He also discusses the possible ways in which the sulfur of the complex that is split off is bound, and how the remaining sulfur could unite in the protein molecule. Goldman and Baumann<sup>7</sup> were able to remove 68% of the sulfur of cystine as lead sulfide when cystine was heated with 10% sodium hydroxide solution in the presence of lead acetate. Suter<sup>5</sup> also studied the effects of heating proteins with sodium hydroxide and noted the similarity of their behavior to that of cystine when treated in the same manner. When he increased the time of heating he obtained as high as 83% of the sulfur of cystine as lead sulfide. Schulz<sup>3</sup> reviewed the work of these investigators and said the lack of agreement of some of the work was due to the fact that part of the sulfur was oxidized during the long heating. In order to avoid this he added zinc to the sodium hydroxide solution and then was able to account for only 53% of the sulfur in cystine after heating with 30% sodium hydroxide for 25 hours. Osborne<sup>10</sup> used Schulz's method of determining loosely and firmly bound sulfur in an endeavor to get at the size of the protein molecule. He analyzed a large number of proteins and found that the percentage of loosely bound sulfur varied from 66% in serumalbumin to 13% in casein.

The question concerning the possible forms of sulfur in proteins is one of importance. The fact that all the sulfur in proteins does not react in the same manner, when the protein is heated with sodium hydroxide, points towards the sulfur being in two different combinations, but on the other hand pure cystine behaves in so much the same manner that definite proof for more than one form of sulfur is not established.

Mörner<sup>11</sup> attempted to answer the question as to whether the sulfur linkage represented by cystine is the only one to be dealt with in proteins. He found that about the same percentage of sulfur was split off from cystine by heating with alkali as was obtained by treating horn, hair, serum globulin and serum albumin under identical conditions.

<sup>8</sup> Fleitmann, *Ann.*, 61, 121 (1847); *ibid.*, 66, 380 (1848).

<sup>9</sup> Danielewski, *Z. Chem.*, 5, 41 (1869).

<sup>6</sup> Danielewski, *Z. physiol. Chem.*, 7, 427 (1883).

<sup>7</sup> Krüger, *Pflüger's Arch.*, 43, 244 (1888).

<sup>7</sup> Goldman and Baumann, *Z. physiol. Chem.*, 12, 254 (1888).

<sup>5</sup> Suter, *ibid.*, 20, 564 (1895).

<sup>3</sup> Schulz, *ibid.*, 25, 16 (1898).

<sup>10</sup> Osborne, *Report Conn. Agr. Exp. Sta.*, 1900, p. 443.

<sup>11</sup> Mörner, *Z. physiol. Chem.*, 34, 207 (1901).

Also, in solutions from which cystine had been separated he found a considerable amount of sulfur which behaved in a manner similar to cystine when treated with alkali, but this substance was not definitely identified. From the experimental results Mörner calculated the percentage of cystine in these proteins and accounted for almost all of the sulfur as being in the form of cystine. As he could account for only a small amount of the sulfur in the membranes of eggs, ovalbumin and fibrinogen as cystine, he concluded that the sulfur of these proteins must be present in other forms. As confirmation of this idea he observed that about  $\frac{1}{3}$  of the sulfur was lost by the volatilization of a sulfur compound. He did not identify this but said that it is possible that  $\frac{1}{3}$  of the sulfur was present in the form of a volatile substance and that it is not impossible that sulfur of these proteins is bound in 3 forms.

The fact that the amount of sulfur split off by alkali differs considerably in the proteins examined also points towards different sulfur forms. Osborne<sup>10</sup>, as noted above, obtained from 13% to 66% of the sulfur, in various proteins, as the sulfide, by boiling with sodium hydroxide. Suter<sup>8</sup> by heating cystine for 9 hours was able to split off 60% of the sulfur, while by heating hair under the same conditions for 15 hours, 98.8% of the sulfur was split off. Pick<sup>12</sup> made the interesting observation that the albuminoses prepared from fibrin gave up the whole of their sulfur as hydrogen sulfide. He concludes that the sulfur must not be present in the form of cystine. While working with koinin,<sup>13</sup> Hofmann and Pregl<sup>14</sup> observed that when this protein was digested with alkali and lead acetate, lead sulfide was formed. They were unable to isolate cystine from the hydrolytic products. Buchtala,<sup>15</sup> however, later isolated 0.5 g. of pure cystine from 100 g. of koinin.

Johnson<sup>16</sup> criticizes the fact that much stress is still laid on the fact that cystine sulfur and protein sulfur react similarly when heated with alkali and consequently the conclusion is accepted that cystine is the source of the loosely bound sulfur in these natural substances, and also that investigation has been focused almost exclusively on the cystine molecule and no careful consideration has been given to the possibility that there may be other unstable sulfur groupings in some proteins, which on hydrolysis can break down, giving hydrogen sulfide. In regard to this he states, "The fact that cystine behaves like a sulfur protein when heated with alkali, or that other primary sulfur cleavage products have not been isolated, does not preclude the possibility of there being other sulfur combinations which can disintegrate to give hydrogen sulfide. This assumption is worthy of some consideration and cannot be excluded from the discussion of this important question. It is not inconceivable that in the digestion of proteins with alkalies and acids, there may be atomic displacements involving the removal of unsaturated sulfur as in  $-C=S$ , which can even occur before the cleavage of the protein itself and the liberation of the cystine molecule." In summing up his discussion of the work done on the sulfur linkages in proteins, he states, "It therefore appears probable from a consideration of the above evidence that there are other sulfur combinations in proteins besides the cystine group which can break down, on hydrolysis, with the formation of hydrogen sulfide."

Van Slyke<sup>17</sup> found that cystine was destroyed or altered during hydrolysis with hydrochloric acid. He determined the amount not destroyed by precipitating it with phosphotungstic acid and found that after cystine was boiled with 20% hydrochloric

<sup>12</sup> Pick, *Z. physiol. Chem.*, 28, 219 (1899).

<sup>13</sup> The horny keratin-like lining of the gizzards of fowls.

<sup>14</sup> Hofmann and Pregl, *Z. physiol. Chem.*, 52, 448 (1907)..

<sup>15</sup> Buchtala, *ibid.*, 69, 310 (1910).

<sup>16</sup> Johnson, *J. Biol. Chem.*, 9, 439 (1911).

<sup>17</sup> Van Slyke, *ibid.*, 10, 15 (1911).

acid for 24 hours only 50% was precipitated by phosphotungstic acid. He states, "It appears possible that the cystine is partially destroyed during the hydrolysis. The results show that this is the case,—the cystine is gradually altered during the hydrolysis, into a substance or substances which are not precipitated by phosphotungstic acid."

Plimmer<sup>18</sup> finds that cystine is decomposed by prolonged boiling with acid. In preparing cystine from wool or hair he obtained the best yield by boiling the material with conc. hydrochloric acid for 3–4 hours. The yield was very poor when the material is boiled for 5–8 hours. He also found a loss when cystine was purified by boiling with charcoal in an acid solution and if boiled for a long time in dilute acid it became yellow or yellow-brown in color. He further states, "Cystine is much more unstable to acid than one is led to expect from the description of its isolation."

Gortner and Holm<sup>19</sup> found that cystine, when mixed with a number of other amino acids, both with and without the addition of formaldehyde, and boiled with 20% hydrochloric acid for 24 hours, was very slightly deaminized. Their results show that if all of the ammonia nitrogen was calculated as being derived from the cystine, only about 2.7% of the cystine amino nitrogen has been changed to ammonia nitrogen. They state, "Cystine was not readily deaminized under the conditions of the experiment."

**The Crystal Form of Cystine as Influenced by Chemical Treatment.**—Mörner<sup>20</sup> noted that the crystals of cystine were different when horn was hydrolyzed for different lengths of time. When horn was heated for one week with hydrochloric acid, he obtained the typical hexagonal plates which have strong optical rotation. When he heated the horn for 2 weeks he obtained very few hexagonal plates, the greater part crystallizing in needles which were optically almost inactive. He describes these as being long needles or long, very thin or narrow, pointed plates which often accumulated in groups. Some resemble tyrosine while others are like small dust particles. He also states that some appeared as thin plates of rhombic form, perhaps with the sharp corners cut off. Mörner was not able to prepare this substance pure, inasmuch as his preparation always contained some of the hexagonal plates. He found no difference in the reaction of the two forms with acids and alkalis. The needle cystine was more soluble in cold water than the plate cystine and was more soluble in hot water than in cold water. Both gave lead sulfide when heated with alkali and lead acetate.

Rothera<sup>21</sup> when preparing cystine found, as did Mörner, that needles were present with the plates and the quantity of needles increased with the length of hydrolysis. He found no difference in the yield of cystine if the hydrolysate was boiled for 18 or 180 hours. He states, "The first recrystallization showed tyrosine-like crystals but after the second, the crystals resemble lecithin spheres. They give the cystine color tests and the required sulfur and nitrogen content." Neuberg and Mayer<sup>22</sup> state that boiling sulfuric acid decomposes cystine much more readily than does hydrochloric acid.

Neuberg and Mayer<sup>23</sup> heated "stone" cystine with hydrochloric acid in a sealed tube at 165° for 14 hours. The resulting product was optically inactive and formed a white amorphous powder. In another article<sup>24</sup> they state that when protein cystine is treated as above, an inactive, needle-like, crystalline substance is obtained. In this article they compare the active and inactive protein cystine and find them quite different. They give the possibilities of this inactive cystine being either a meso-cystine or a racemic mixture.

<sup>18</sup> Plimmer, *Biochem. J.*, 7, 311 (1913).

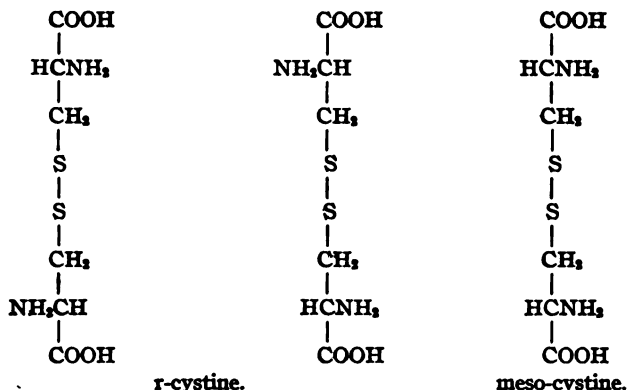
<sup>19</sup> Gortner and Holm, *THIS JOURNAL*, 42, 821 (1920).

<sup>20</sup> Mörner, *Z. physiol. Chem.*, 28, 595 (1899).

<sup>21</sup> Rothera, *J. Physiol.*, 32, 175 (1905).

<sup>22</sup> Neuberg and Mayer, *Z. physiol. Chem.*, 44, 98 (1905).

<sup>23</sup> Ref 22, p. 472.



They were able to prepare the inactive cystine from the inactive cystine. This was completely inactive and analyzed for cystine. They grew *Aspergillus niger* on some of the inactive cystine and obtained a cystine that was dextrorotatory. It was suggested that this method might be used to prepare pure *d*-cystine. To quote them concerning the crystal form of this preparation: "It is noteworthy that our purest *d*-cystine ( $[\alpha]_D = +93.78^\circ$ ) forms microscopical six-sided plates as well as needles. The theory required that *d* and *l* cystine should be enantiomorphous."

**The Synthesis of Cystine.**—Erlenmeyer<sup>24</sup> synthesized cystine from benzoyl serin ester. He does not state whether the material was completely inactive nor does he note the crystalline form. Erlenmeyer and Stoop<sup>25</sup> again prepared cystine from benzoyl serin ester and phosphorus pentasulfide. They first obtained cystein which they oxidized to cystine. In regard to the yield and description of the product, they state, "Thus one obtains cystine in a 40% yield as a granular microcrystalline powder. After repeated solution in ammonia and reprecipitation by acetic acid the cystine is pure and forms stellate groups of needles. The only difference between the synthetic and the natural product is that the solution of the former does not show optical rotation. A solution of 0.5 g. of the synthetic cystine in hydrochloric acid in a 2cm. tube gave no rotation of the polarized light."

Fischer and Raske<sup>26</sup> prepared *d-l*-cystine from *d-l*- $\alpha$ -amino- $\beta$ -chloro-propionic acid and describe it thus: "After some time the cystine separated as a colorless mass of very tiny crystals, which under the microscope appeared on first glance to be more or less spherical masses but which were resolved into needles or very thin prisms." The analysis of this preparation agreed quite well with that of plate cystine. They also prepared the *l*-cystine from *l*- $\alpha$ -amino- $\beta$ -chloro-propionic acid. This preparation was optically active  $[\alpha]_D^{20} = 209.6^\circ \pm 1^\circ$ . Their analyses show this to be identical in chemical composition with plate cystine. Concerning the crystalline form of this preparation, they state: "Our synthetic product has a very different crystal form, the preparation precipitated from an ammoniacal solution with acetic acid forms microscopic tiny, apparently right-angled, prisms or perhaps many-faced crystals."

It is interesting to note that *cystine crystallizing in hexagonal plates has never been synthesized* and in view of Neuberger and Mayer's<sup>27</sup> experiments, the question arises as to whether the cystine actually synthesized may not be "stone" cystine, providing that "stone" cystine actually does differ from "protein" cystine.

<sup>24</sup> Erlenmeyer, *Ber.*, 36, 2720 (1903).

<sup>25</sup> Erlenmeyer and Stoop, *Ann.*, 337, 236 (1904).

<sup>26</sup> Fischer and Raske, *Ber.*, 41, 893 (1908).

### Experimental.

**The Problem.**—In view of the varied opinions referred to under "Historical," it seemed desirable to test the effect of prolonged boiling with hydrochloric acid on cystine with special reference to the behavior of cystine in a protein hydrolysis. Many investigators appear to believe that cystine is destroyed either in whole or in part during acid hydrolysis. This idea is upheld by the work of Van Slyke<sup>17</sup> and Plimmer.<sup>18</sup> Gortner and Holm<sup>19</sup> show, however, that in a mixture of pure amino acids, cystine is not easily de-aminized during acid hydrolysis. From the work of Mörner,<sup>20</sup> Rothera<sup>21</sup> and Neuberg and Mayer<sup>22</sup> it seems probable that cystine may be completely changed to an isomeric cystine during long acid hydrolysis. As most of the work carried out to study the effects of acid hydrolysis has been done on proteins and since the relation of the cystine content to the sulfur content is still uncertain, it seemed desirable to carry out a prolonged acid hydrolysis on cystine alone, and follow the possible types of decomposition by analysis after boiling for different lengths of time.

There are several possible changes, one or more of which might take place when cystine is boiled for a long time with hydrochloric acid. Several of the most probable were followed by removing aliquots at definite intervals and performing certain analyses. The possible changes followed during the boiling were: (1) the loss of carbon dioxide which might be formed by decarboxylation; (2) the loss of hydrogen sulfide which might result from a splitting of the —S—S— union and a subsequent evolution of hydrogen sulfide; (3) some of the sulfur might be oxidized to sulfate; (4) a loss of total sulfur in the hydrolysate due to the formation of volatile sulfur compounds; (5) the amount of unoxidized sulfur as determined by the potassium bromate method of Okuda;<sup>21</sup> (6) the amount of nitrogen precipitated by phosphotungstic acid; (7) the amount of total nitrogen, which might be altered by the evolution of elementary nitrogen or the formation of volatile nitrogen-containing substances; (8) the amount of amino nitrogen, which might decrease due to deaminization; (9) the formation of ammonia nitrogen as a result of deaminization; (10) the specific rotation of the acid solution of cystine; (11) the isolation of the organic compounds present in the solution after the prolonged boiling and the comparison of their properties with those of cystine, in order to determine the extent and direction of the decomposition or alteration of cystine under the conditions of the experiment.

**The Material.**—For an experiment of this type, a large amount of cystine is required. After several methods had been tried, a slight modification of Folin's method<sup>27</sup> was used.

Human hair or wool (human hair, which can be obtained without difficulty at almost any barber shop, is preferable) is washed in cold dilute (1% or 2%) sodium

<sup>27</sup> Folin, *J. Biol. Chem.*, 8, 9 (1910).

carbonate solution and dried. This washing is to remove the natural oils from the hair. Two kg. of the dry, washed hair is pushed into a 6-liter Pyrex flask (round-bottom preferable) and 4 liters of constant boiling (20%) hydrochloric acid is added. In order to get some of the acid quickly to the bottom of the flask, part of the acid may be added first, then the hair, and finally the remaining acid. It is sometimes convenient to heat the acid and dissolve a part of the hair before all is added. The hair is hydrolyzed by boiling the contents of the flask over a free flame or better on a sand-bath; or by heating on a steam-bath until the biuret reaction is entirely negative. This is negative after boiling for about 4 hours or heating on a steam-bath for 5-6 days. A reflux condenser should be used if the hydrolysate is boiled but if the steam-bath method is employed an air condenser is equally efficient. The flask is then removed from the steam-bath and the solution of amino acids *almost neutralized* with conc. sodium hydroxide (commercial 98%) solution and then sodium acetate solution is added until the congo red test for mineral acids is entirely negative. *Care must be taken not to make the solution alkaline with sodium hydroxide.* After standing for 48 to 72 hours at room temperature, the liquid is filtered from the precipitated cystine. This can be best accomplished on a Büchner funnel, using suction. The crude material, containing in addition to the cystine some "humin," melanin and tyrosine, is dissolved in 3% hydrochloric acid and completely decolorized with a vegetable decolorizing carbon or with good bone-black which has been completely freed from calcium phosphate by boiling with hydrochloric acid and washing with cold water. The filtrate after decolorizing should be water clear or at the most only a faint straw color. If it shows much color the treatment with decolorizing carbon should be repeated. The cystine is precipitated from this clear solution using first sodium hydroxide to weakly acid reaction followed by sodium acetate. After standing for at least 6 hours, the cystine is filtered off and washed with hot water, which will remove the last traces of tyrosine.

By this method, with very little work, the typical, colorless, hexagonal plates of cystine are obtained. With human hair the yield is about 100 g., or 5%.

**The Methods.**—For carrying out a study as outlined above, an apparatus as shown in Fig. 1, was used.

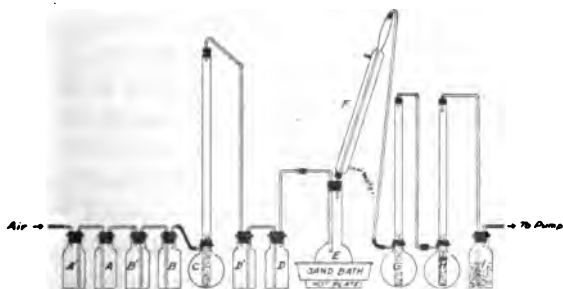


Fig. 1.

A' is an empty wash bottle connected to A by means of a glass tube reaching from the bottom of A' to the bottom of A. This serves as a trap in case of back pressure.

A is a wash bottle containing lead acetate to remove any traces of hydrogen sulfide in the air.

B' is a trap to B connected as A' and A.

B is a wash bottle containing 50% potassium hydroxide solution to remove the carbon dioxide from the air.



C is an absorption tower as described by Truog<sup>28</sup> excepting that a round-bottom flask is used. This contained a saturated solution of barium hydroxide and was placed in the series as B alone did not remove all of the carbon dioxide from the air.

D' is a trap to D connected as A' and A.

D is a wash bottle containing 20% hydrochloric acid to remove any ammonia from the air and to wash the air before it was drawn into flask E.

E is a round-bottom, 2-liter flask in which the hydrochloric acid and cystine were placed during the boiling. The flask was placed on a sand-bath and heated by means of an electric hot-plate.

F is a water-cooled condenser.

G is an absorption tower containing cadmium sulfate. This absorbs the hydrogen sulfide drawn through by the air.

H is another absorption tower containing barium hydroxide. This absorbs the carbon dioxide as it is drawn through by the air.

K is a tube containing soda lime to prevent carbon dioxide from entering the apparatus.

To 50 g. of cystine (97.5% pure, containing 2.5% of ash and moisture) enough constant-boiling hydrochloric acid was added to make a total volume of 1000 cc. This was placed in flask E and the flask and contents weighed to 0.01 g. on a large analytical balance (sensitive to 1 mg. and having a capacity of 1500 g.). The flask was connected as shown in Fig. 1, the cadmium sulfate placed in Tower G and the apparatus washed free from carbon dioxide by drawing carbon dioxide-free air through it for a few minutes. The barium hydroxide was then placed in Tower H. Washed air was drawn through the apparatus by means of a water pump. The rate was very slow until just before the aliquot was removed; then the flow of air was increased so that all of the carbon dioxide and hydrogen sulfide might be washed out in a short time. After the solution had boiled for 3 hours and the carbon dioxide and hydrogen sulfide had been washed out of the apparatus, the solutions in Towers G and H were titrated as described below. The flask E was disconnected, the contents cooled to room temperature and made up to the *original weight* with 20% hydrochloric acid. A 50cc. aliquot, containing 2.5 g. of the original cystine or 2.4375 g. of pure cystine, was removed and made up to 250 cc., this being used in subsequent analyses. The flask and contents were again weighed and the process repeated. Aliquots were removed at the end of 3, 6, 12, 24, 48, 96, 144 and 192 hours and the samples numbered 3, 6, 12, etc.

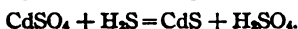
The following methods were used in the analysis of the samples removed at the different intervals.

1. Carbon dioxide. This was determined by placing 25 cc. (or 50 cc. in the last two determinations, 144 and 192 hours) of approximately 0.125 *N* barium hydroxide in Tower H. After the heating was discontinued and the apparatus washed free from carbon dioxide, the remaining barium hydroxide was titrated with hydrochloric acid, using phenolphthalein as an indicator. As the strength of the barium

<sup>28</sup> Truog, *J. Ind. Eng. Chem.*, 7, 1045 (1915).

hydroxide was known in terms of the standard acid, the amount of carbon dioxide was calculated from the difference in the amounts of acid used.

2. Hydrogen sulfide. The principle of this determination is described by Scott.<sup>29</sup> It is based on the fact that when hydrogen sulfide comes in contact with a solution of cadmium sulfate, the following reaction takes place,

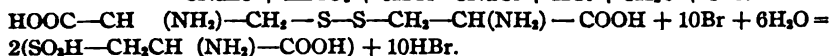


The sulfuric acid thus formed is titrated with a standard alkali. For this determination a solution of cadmium sulfate containing 24 g. per liter was neutralized with sodium hydroxide, using sodium alizarine sulfonate as an indicator. Twenty-five cc. of this solution (or 50 cc. in the last three determinations, 96, 144 and 192 hours), was placed in Tower G. This tower was removed as described for Tower H and the sulfuric acid formed was titrated. In order to determine the amount of the acidity due to hydrochloric acid which may have been aspirated over into the cadmium sulfate solution from the constant-boiling hydrochloric acid, the solution after neutralization was titrated with standard silver nitrate solution, using potassium chromate as an indicator. In no instance was there an appreciable amount of hydrochloric acid present.

3. The sulfur that might be present in the sulfate form was determined by adding a small amount of conc. hydrochloric acid to 20 cc. of the solution and heating to boiling. Five cc. of 10% barium chloride was slowly added and the barium sulfate weighed in the usual manner. From the weight of barium sulfate the amount of sulfate sulfur was calculated.

4. Total sulfur was determined in 10 cc. of the solution by oxidizing to sulfate with 10 cc. of the oxidizing reagent described by Denis.<sup>30</sup> The solution of cystine and oxidizing agent is evaporated to dryness on a steam-bath, ignited at red heat for 10 minutes, cooled and the residue dissolved with hot 10% hydrochloric acid. The sulfate was precipitated out of the boiling solution by means of barium chloride and the sulfur calculated from the amount of barium sulfate formed.

5. The amount of cystine present as determined by the potassium bromate method was carried out as described by Okuda,<sup>31</sup> according to the equations



To 10 cc. of the cystine solution, enough hydrochloric acid is added to make a 5 to 10% solution. To this, 10 cc. of 20% sodium bromide solution is added and the solution titrated with 0.05 *N* potassium bromate solution, the end-point being the first faint yellow color (free bromine) that persists for one minute. One cc. of the sodium bromate solution is equivalent to 0.00721 g. of cystine. When this method was used on pure cystine the results checked with the sulfur and nitrogen determinations.

6. The amount of nitrogen not precipitated by phosphotungstic acid was determined by the method previously used by Van Slyke.<sup>17</sup> Ten cc. of the solution was placed in a 100cc. volumetric flask, 10 cc. of conc. hydrochloric acid and 5 g. of phosphotungstic acid were added and the solution was made up to volume. After the phosphotungstic acid had dissolved, the flask was placed in a refrigerator for 24 hours. The supernatant liquid was then carefully decanted through a dry filter and the amount of nitrogen in an aliquot from the filtrate was determined by the Kjeldahl method, and, as the amount

<sup>29</sup> Scott, "Standard Methods of Chemical Analysis," D. Van Nostrand Co., New York, 2nd Ed., pp. 398-403.

<sup>30</sup> Denis, *J. Biol. Chem.*, 8, 401 (1910).

<sup>31</sup> Okuda, *J. Coll. Agr. Imp. Univ. Tokyo*, 7, No. 1, 69 (1919).

of total nitrogen in 100 cc. was known, the difference represented the amount of nitrogen in the precipitate.

7. Total nitrogen was determined by the Kjeldahl method.

8. Amino nitrogen was determined by the Van Slyke apparatus<sup>22</sup> for determining amino nitrogen.

9. Ammonia nitrogen was determined on a 20cc. portion of the solution. This was placed in a distilling flask with 100 cc. of water and the solution made slightly alkaline with calcium hydroxide; 100 cc. of alcohol was added and the ammonia distilled at 40–45°, under reduced pressure, into standard sulfuric acid.

10. The specific rotation of the acid solution was determined by means of a high grade Schmidt and Haensch polariscope.

### The Experimental Data.

**A. The Decomposition of Cystine on Boiling with 20% Hydrochloric Acid for Various Lengths of Time.** *The Hydrolysis.*—When heating began the cystine hydrochloride was not all in solution, but at the end of 3 hours' boiling the cystine hydrochloride had completely dissolved. Very little change in appearance was observed during the first 12 hours except that the color of the solution became somewhat yellow and a small amount of sulfur crystallized on the neck of the flask. After 24 hours the solution was deep yellow, a flocculent precipitate began to separate and a considerable amount of sulfur had crystallized on the neck of the flask and in the condenser tube. At 48 hours a very pungent odor was noticed when the flask was opened: the solution was yellow-brown in color and a white substance was deposited on the lower part of the flask or else a substance was formed during the boiling that had etched the glass. During 48 to 144 hours the solution became darker and murky, the amount of flocculent precipitate increased and some of the sulfur in the condenser washed back into the flask. At the end of the boiling the solution was a dirty brown color and gave off a very pungent, irritating odor. The lower part of the flask was covered with a white, insoluble substance or was etched so as to be perfectly opaque.

It was of interest to note that cystine when boiled with acid for a long time deposits sulfur on the neck of the flask and in the condenser, as do proteins when treated in a similar manner. Mörner<sup>20</sup> found that when horn was hydrolyzed with hydrochloric acid for a short time little or no free sulfur was formed, but when the heating was continued for a long time, a not inconsiderable amount of sulfur separated. Buchtala<sup>18</sup> observed that some proteins when hydrolyzed deposited sulfur, while others did not.

*The Carbon Dioxide Determinations.*—The analytical data are shown in Table I. From the results given in this table, it is evident that very little decarboxylation takes place. The carbon dioxide undoubtedly comes from the slow decomposition of cystine and not from a change in the

<sup>22</sup> Van Slyke, *J. Biol. Chem.*, 9, 185 (1911).

cystine molecule. The large amount given off at the end of the first 3 hours may be due to the acid solution of cystine containing dissolved carbon dioxide, since it was not boiled before the experiment was started.

*The Sulfur Determinations.*—The amount of sulfur given off as hydrogen sulfide is shown in Table II. This table shows that only a small amount of the sulfur is evolved as hydrogen sulfide during the prolonged boiling with acid. Here, as in the carbon dioxide determination, the only source of error is that a volatile acid may have been formed that would be absorbed by the cadmium sulfate and titrated as sulfuric acid. There is proof, however, that hydrogen sulfide was formed, for the characteristic yellow precipitate of cadmium sulfide was produced in a not inconsiderable quantity. The amount of hydrogen sulfide given off, like the amount of carbon dioxide, does not point toward any changes in the cystine molecule but toward a slow decomposition of the cystine. Mörner<sup>20</sup> observed that when keratin was heated with hydrochloric acid, for a long time, hydrogen sulfide was evolved.

The results for the sulfur oxidized to sulfate, Table II, show that apparently a very small amount of sulfate is present and that the amount is constant during the hydrolysis. This indicates that no appreciable oxidation of sulfur to sulfate has taken place and that the substance weighed as barium sulfate is probably the ash contained in the original cystine. The amount is so small that it can be disregarded.

The amount of total sulfur serves as a check on the amount of sulfur in the solution but does not show the amount of cystine. Some elementary sulfur was deposited on the neck of the flask and in the condenser tube. In the earlier aliquots this would not be accounted for in the "total sulfur" figures. This sulfur later washed down and increased the total sulfur values in later determinations. The results in Table II show that the amount of total sulfur decreases until 144 hours and then increases. As already stated, the sulfur on the neck of the flask and on the condenser tube washed down so that practically none was left at the end of 192 hours. It is also noted that, at the end of the experiment or 192 hours, 17.5 g. of the cystine had been removed, so that part of the sulfur which washed back into the flask came from the cystine in the aliquots that had been removed from the flask. There was a possibility that the flocculent precipitate, noted above, might contain some sulfur. This was confirmed by subsequent analysis, as a sulfur determination made on the 144-hour aliquot after the precipitate had settled, showed that the sulfur content of the filtrate alone was 0.4% lower than when determined on the solution containing the flocculent precipitate. This shows that some of the sulfur had precipitated out of the solution with the settling of the precipitate. The total sulfur determinations do not show what is happening to the cystine molecule. The hydrogen sulfide determinations give the only index

TABLE I  
DECARBOXYLATION OF ALIQUOTS OF CYSTINE BOILED FOR DIFFERENT LENGTHS OF TIME WITH 20% HYDROCHLORIC ACID

	3	6	12	24	48	96	144	192
Carbon dioxide per g. of cystine, <sup>a</sup> ...mg	1.905	2.337	3.077	3.922	5.784	10.839	15.833	23.505
COOH CO <sub>2</sub> ,.....%	0.519	0.637	0.839	1.069	1.577	2.956	4.326	6.410

<sup>a</sup> The calculations were made from the amounts of cystine left in the flask at the end of each interval.

TABLE II  
ANALYSES FOR THE VARIOUS FORMS OF SULFUR IN ALIQUOTS OF CYSTINE BOILED FOR DIFFERENT LENGTHS OF TIME WITH 20% HYDROCHLORIC ACID

	Original	3	6	12	24	48	96	144	192
Hydrogen sulfide per g. of cystine, <sup>a</sup> ...%	.....	0.075	0.101	0.145	0.229	0.428	1.319	2.280	4.070
Sulfur split off as hydrogen sulfide,....%	.....	0.028	0.038	0.054	0.086	0.160	0.494	0.855	1.526
Sulfate-sulfur per g. of cystine,....mg	.....	0.840	1.050	1.050	1.260	0.840	0.770	1.400	0.840
Sulfur as sulfate,.....%	.....	0.315	0.394	0.394	0.472	0.315	0.289	0.525	0.315
Total sulfur per g. of cystine,.....mg	265.4	269.6	263.6	250.4	255.4	250.4	250.9	258.5	259.1
Total sulfur in original cystine,....%	26.54	25.96	25.36	25.04	25.54	25.04	25.09	25.85	25.91

<sup>a</sup> The calculations were made from the amounts of cystine left in the flask at the end of each interval.

TABLE III  
AMOUNT OF CYSTINE BY THE BROMATE METHOD IN ALIQUOTS BOILED FOR DIFFERENT LENGTHS OF TIME WITH 20% HYDROCHLORIC ACID<sup>a</sup>

	Original	3	6	12	24	48	96	144	192
Cystine per g. of original cystine,....mg	1000.40	970.90	951.80	948.00	939.90	925.20	953.20	971.10	905.80
Cystine,.....%	100.04	97.09	95.18	94.80	93.99	92.52	95.32	97.11	90.58

<sup>a</sup> See text for a possible explanation of the discordant results for 96 and 144 hours.

as to what becomes of a small part of the sulfur while the sulfate determinations show that none of the sulfur is oxidized to the sulfate.

*The Amount of Cystine as Determined by the Potassium Bromate Method.*—The results given in Table III show that the sulfur in cystine is not readily oxidized by boiling with acid under the conditions of this experiment; at any rate, most of the sulfur still reacts with bromine. The end-points were very indistinct after 24 hours, when the color of the solution was almost that of the end-point, therefore making it very difficult to obtain accurate titrations. It is readily seen that for colored solutions the bromate method is of little or no value as a quantitative method but serves as a qualitative method, showing that the sulfur in the cystine is still largely in an unoxidized form.

*The Nitrogen Precipitated by Phosphotungstic Acid.*—The amounts of nitrogen not precipitated by phosphotungstic acid are given in Table IV. The data are given in this form rather than subtracting from the total nitrogen which would give the amounts precipitated by phosphotungstic acid. The amount of nitrogen not precipitated increases until the cystine has been boiled for 48 hours and then the values remain practically constant for the longer periods of boiling. After 48 hours no more of the typical crystalline cystine phosphotungstate precipitate as formed with protein (plate) cystine was obtained, but instead a more granular and amorphous precipitate formed. The precipitates of 96, 144 and 192 hours all looked alike and contained about the same quantity of the precipitate while from the "original" to 48 hours, the amount of precipitate decreased and contained less of the typical crystalline plate cystine precipitate. This indicates that the cystine has been changed in some respect making the phosphotungstic acid precipitate more soluble or changing it into a form that is not precipitated by phosphotungstic acid. Van Slyke<sup>17</sup> found that under our conditions of precipitation, 1.5 mg. of nitrogen per 100 cc. was not precipitated when pure cystine was used, but with cystine which had been boiled with 20% hydrochloric acid for 24 hours, he found that about 7 mg. of nitrogen per 100 cc. of the solution was not precipitated by phosphotungstic acid.

*The Nitrogen Determinations.*—The total nitrogen, Table V, merely serves as a check on the amount of nitrogen in the solution. It shows that very little, if any, nitrogen was lost in the form of a volatile substance during the long boiling with acid. The total nitrogen determinations do not show any change in the form of the nitrogen.

The amino nitrogen figures, Table V, are not very consistent. Even when they are multiplied by the factor 0.926, used for cystine nitrogen when determined in the Van Slyke apparatus,<sup>32</sup> they give a higher result than the total nitrogen values. There is a possibility that the amount of substance, causing the high amino nitrogen values when cystine is de-

TABLE IV  
NITROGEN NOT PRECIPITATED BY PHOSPHOTUNGSTIC ACID, PER 100 CC. OF SOLUTION, FROM ALIQUOTS OF CYSTINE BOILED FOR DIFFERENT LENGTHS OF TIME WITH 20% HYDROCHLORIC ACID

	Hours' Boiling						
	Original	3	6	12	24	48	96
Nitrogen not precipitated,.....mg.	1.20	1.92	2.92	4.16	5.04	6.08	6.12
Nitrogen not precipitated,*.....%	10.29	16.46	25.04	35.68	43.22	52.14	52.49

\* Calculated, 11.66 mg. of nitrogen in 100 cc. of solution.

TABLE V  
ANALYSES FOR THE VARIOUS FORMS OF NITROGEN IN ALIQUOTS OF CYSTINE BOILED FOR DIFFERENT LENGTHS OF TIME WITH 20% HYDROCHLORIC ACID

	Hours' Boiling						
	Original	3	6	12	24	48	96
Total nitrogen per g. of original cystine,.....mg.	114.8	112.30	110.50	111.60	111.70	111.50	111.50
Amino nitrogen per g. of original cystine,.....	129.0	137.70	131.00	131.50	129.80	129.30	127.60
Ammonia nitrogen per g. of original cystine,.....	.....	2.35	2.56	2.66	3.28	3.28	3.69
Total nitrogen as ammonia nitrogen,*.....%	.....	2.02	2.19	2.28	2.81	2.81	3.16

\* Calculations made on the basis of pure cystine, nitrogen = 11.66%.

TABLE VI  
CHANGES IN THE SPECIFIC ROTATION OF ALIQUOTS OF CYSTINE BOILED FOR DIFFERENT LENGTHS OF TIME WITH 20% HYDROCHLORIC ACID

	Hours' Boiling						
	Original	3	6	12	24	48	96
Specific rotation of acid solution,.....	-201.70°	-180.20°	-152.50°	-124.70°	-48.50°	-20.80°	00.00°
Decrease in specific rotation,.....%	0.00	10.66	24.39	38.17	75.95	89.69	100.00

aminized in the Van Slyke apparatus, is increased during the hydrolysis, thus making the error still greater. It is probable that the amount of amino nitrogen actually decreases slightly during the hydrolysis, due to the formation of ammonia.

With the exception of one or two samples, the ammonia nitrogen, Table V, increases almost proportionally to the decrease of amino nitrogen. Gortner and Holm<sup>19</sup> found that when a mixture of amino acids and formaldehyde was boiled for 24 hours with 20% hydrochloric acid very little ammonia was formed. Assuming that all of the ammonia nitrogen in their Expt. No. II came from cystine, only 2.74% of the nitrogen was split off as ammonia. This agrees very well with the results obtained in this experiment where only 2.81% of the nitrogen is in the form of ammonia at the end of 24 hours.

*The Optical Activity of the Acid Solution.*—The specific rotations, Table VI, show that cystine is gradually and completely changed into an inactive substance or substances by prolonged acid hydrolysis. The greatest change takes place during the first 48 hours and *at 96 hours the solution is completely inactive*. Mörner<sup>11</sup> observed that when cystine was heated on a steam-bath for 109 hours with 10% hydrochloric acid, the specific rotation changed from  $-223^{\circ}$  to  $-134^{\circ}$  and the cystine was changed to a more soluble form. As to our original rotation of  $-201.7^{\circ}$  as compared with that of  $-223^{\circ}$  usually given for cystine, one can easily see from the specific rotations that cystine is very easily changed by acid hydrolysis to an inactive form, and we believe that it is almost impossible to prepare pure plate cystine with maximum optical rotation by any method which involves heating for any considerable period of time in a strong acid solution. Mörner, in his first paper on the preparation of cystine, realized the fact that it is almost impossible to obtain two preparations with identical optical rotations.

From these results, one concludes that only a small amount of the cystine is *decomposed* during prolonged boiling with acid, as measured by production of ammonia, carbon dioxide, or hydrogen sulfide or by changes in unoxidized sulfur. The major portion of the cystine is apparently *changed* into a form that is optically inactive and is not as completely precipitated with phosphotungstic acid as is plate cystine. We therefore attempted to isolate the organic compound which remained in the solution after 196 hours of boiling.

**B. The Isolation of an "Isomeric" Cystine from the Residual Solution.**  
*Isolation and Analysis.*—After the residual solution had stood for 28 days, the flocculent precipitate noted in the previous section was filtered off, washed with 20% hydrochloric acid and dried. It was grayish-black in color. The black portion was soluble in hot water, and after the water was evaporated a jet black residue remained. A part of the precipitate



was extracted with carbon disulfide to remove any elementary sulfur. When the carbon disulfide was evaporated the characteristic yellow crystals of sulfur remained. The residue from the carbon disulfide extraction was extracted with hot water. The insoluble portion contained some inorganic matter besides a very small amount of organic matter. An analysis of the black water-soluble portion of the original precipitate gave amino nitrogen, 7.73%; total nitrogen, 15.89%; and total sulfur, 8.73%. This analysis shows that this residue is not cystine but probably some decomposition product. Only a very small quantity was obtained, not sufficient in amount for further experimental work.

The filtrate from the flocculent precipitate was evaporated to dryness *in vacuo* on a boiling water-bath, and then held at 100° *in vacuo* until the excess of hydrochloric acid was driven off. Flaky, needle-like crystals were formed. These were then dissolved in water and a portion of the solution was removed for analysis. The amounts of total nitrogen, amino nitrogen and total sulfur were determined. The ratio of nitrogen to sulfur was almost identical with the ratio for cystine.

Mg. in 10 cc.	Mg. in 10 cc.
Amino nitrogen = 12.96 (corr. for cystine according to Van Slyke <sup>22</sup> )	Total sulfur = 30.00
Total nitrogen = 12.96	Ratio N:S = 1:2.31 (ratio for cystine = 1:2.29).

In the hope of precipitating cystine from the solution, sodium acetate was added until no more free hydrochloric acid was present. A voluminous precipitate settled out. The filtrate from this precipitate was again analyzed for total nitrogen, amino nitrogen and total sulfur.

Mg. in 10 cc.	Mg. in 10 cc.
Amino nitrogen = 4.92 (corr. for cystine)	Total sulfur = 10.60
Total nitrogen = 5.03	Ratio N:S = 1:2.11.

These data show that there was probably only one substance present in any appreciable amount in the original solution, for the ratio of the amino nitrogen to the total nitrogen and to the total sulfur in the filtrate before precipitating with sodium acetate and after precipitating is about the same.

The precipitate was filtered off, dissolved in dil. hydrochloric acid, decolorized with acid-extracted bone black and the substance precipitated with sodium acetate from the colorless solution. The precipitate was washed free from sodium acetate, dried at 100° and analyzed.

	Found %	Calculated for cystine %
Amino nitrogen.....	11.65 (corr.)	11.66
Total nitrogen.....	11.56	11.66
Total sulfur.....	26.83	26.69

These figures show that during the long boiling the composition of cystine has not been changed.

*Physical Properties.*—This "isomeric" cystine consists of white, powdery crystals which at first look like solid spheres somewhat resembling the

crystal balls of tyrosine, but after a time the crystal form appears to be very fine short needles. Under a high power microscope (preferably oil immersion) these do not prove to be needles but thin, blunt prisms, while the plate cystine consists of large, hexagonal plates. This is undoubtedly the same crystal form that Mörner<sup>20</sup> and Rothera<sup>21</sup> observed in their preparations of plate cystine prepared from keratin by prolonged acid hydrolysis. The average length of the prism crystals is probably about 1/20 of the average diameter of the plate crystals. The cross section of the prism crystals is extremely minute. *These crystals compare very well with the description which Erlenmeyer<sup>25</sup> and Fischer and Raske<sup>26</sup> gave for their synthetic preparations of inactive cystine and also for the l-cystine prepared by Fischer and Raske.*

This "isomeric" cystine is optically inactive; a 1.0 g. dissolved in 25 cc. of dil. hydrochloric acid and placed in a 2cm. tube gave no optical rotation. It is insoluble in hot or cold alcohol, appreciably soluble in hot water and more soluble in cold water than is the plate cystine. When this "isomeric" cystine is boiled with conc. sodium hydroxide and lead acetate, lead sulfide is formed.

**Solubility.**—The relative solubility of the two forms of cystine was determined as follows. 200 cc. of carbon dioxide and ammonia-free water and 1 g. of cystine were placed in a glass container. This was agitated in a shaking machine for 7 hours. After standing for several days, the solution was filtered by gravity through dry hardened filter paper. Fifty cc. of the filtrate was placed in a weighed platinum dish, evaporated on a steam-bath, dried at 100° and weighed. The solubility of the glass from the containers was also determined by using water alone and carrying out the procedure described above. This "blank" was then subtracted from the result obtained when cystine was used. The solubility in pure water at 20° is 1 g. in 5263 parts of water for plate cystine and 1 g. in 2059 parts of water for "isomeric" cystine. These results show that the "isomeric" cystine is 2.556 times as soluble as is the plate cystine. Neuberg and Mayer<sup>22</sup> give the solubilities of plate cystine and their "inactive" cystine as 1 : 8840 for the former, and 1 : 3070 for the latter. Their results show that the "inactive" cystine is 2.879 times as soluble as is the plate cystine. The difference in the amount dissolved is probably due to the method of obtaining a saturated solution. They do not state how they obtained a saturated solution of their preparations or how they determined the amount of cystine in solution.

**Precipitability with Phosphotungstic Acid.**—The amount of the "isomeric" cystine precipitated by phosphotungstic acid was compared with the amount of plate cystine precipitated under identical conditions. One-quarter of a gram of the cystine was placed in a 250cc. flask, 25 cc. of conc. hydrochloric acid and 12.5 g. of phosphotungstic acid were added, and the

mixture diluted to 250 cc. and placed in an ice box for 24 hours. Total nitrogen was then determined on aliquots of the filtrate.

The analysis of the filtrate from the plate cystine precipitate showed that under these conditions 1.2 mg. of nitrogen per 100 cc. of the solution was not precipitated by phosphotungstic acid, while the analysis of the filtrate from the "isomeric" cystine precipitate showed 4.82 mg. of nitrogen not precipitated. The phosphotungstate of the "isomeric" cystine is therefore 4 times as soluble as that of the plate cystine. Another difference was noted in the physical state of the precipitates. The "isomeric" cystine precipitate did not contain the typical plate cystine phosphotungstate precipitate but a heavy, granular-like precipitate. The precipitate of the "isomeric" cystine did not form for several hours, while that of the plate cystine formed immediately.

*The Hydrochlorides.*—The difference in the hydrochlorides was shown by making use of the microscopic method described by Doniges.<sup>22</sup> A small quantity of the fine material is placed on a glass slide and a drop of conc. hydrochloric acid is added. This is examined without a cover glass, under a microscope. Crystals of the hydrochloride soon form. The crystals of the plate cystine hydrochloride are long, prismatic needles while those of the "isomeric" cystine hydrochloride are diamond or rectangular shaped prisms or masses of plates. The hydrochlorides of the two forms of cystine are decidedly different, thus forming an easy method of detecting small amounts of either form.

*Organic Derivatives of the Two Compounds.*—We have prepared a number of derivatives of the "isomeric" cystine and plate cystine and have found them to possess entirely different properties. Inasmuch, however, as this comparative study is not complete, a detailed description of the derivatives will be the subject of a subsequent paper.

### Discussion.

It was necessary to discuss each topic at the time the analytical data were presented. There is little need of further extensive discussion.

The data in Tables I–VI show that very little change occurred in aliquots of a cystine solution boiled for various lengths of time with hydrochloric acid. The analyses show that there is but little decomposition that can be measured by the methods used. Three of the possible changes, *i. e.*, ammonia formation, loss of carbon dioxide, and hydrogen sulfide evolution, show a slow progressive decomposition, while the precipitability with phosphotungstic acid and the optical activity show that the cystine undergoes some change that makes the cystine, or the products resulting from the long boiling, optically inactive and the phosphotungstate more soluble. The greatest change takes place during the first 48 hours. At

<sup>22</sup> Doniges, *J. Soc. Pharm. Bordeaux*, 58, 8 (1920); *C. A.*, 14, 1689 (1920).

the most, only about 10% of the cystine was decomposed by boiling for 192 hours.

An "isomeric" cystine was isolated from the residual hydrolysate. This "isomeric" cystine proved to be the principal constituent of the hydrolysate. It was found to be optically inactive, and its phosphotungstate was much more soluble than that of the plate cystine. Certain derivatives of this cystine have been compared with those of plate cystine and these, as do the other comparisons made, show the two forms of cystine to be different. This tends to prove the conclusions one might draw from the first part of the experiment, *i. e., cystine is not appreciably decomposed or destroyed when boiled for a long time with 20% hydrochloric acid but is changed into another compound that is optically inactive and has different physical and chemical properties.* This "isomeric" cystine showed the required amount of amino nitrogen, total nitrogen and total sulfur for cystine. It differs from plate cystine in every comparison made between the two forms of cystine.

Whether or not the "isomeric" cystine is simply a racemic form of the original *L*-cystine has not yet been definitely proved, but in view of the fact that the cystine synthesized by Fischer and Raske<sup>26</sup> and by Erlenmeyer and Stoop<sup>26</sup> crystallized in the form of needles *and the synthetic L-cystine prepared by Fischer and Raske likewise crystallized in the form of needles, it appears possible that the natural L-cystine, crystallizing in hexagonal plates, has never been synthesized* and that we have merely succeeded in changing the natural hexagonal cystine into the needle form. The structural relationships involved in such a change must remain unknown until further experimental work can be carried out. Likewise the nutritional utilization of the "isomeric" cystine is a problem which we intend to study in the near future.

### Summary and General Conclusions.

Cystine was boiled for various lengths of time with 20% hydrochloric acid and analyses made on aliquots at each time interval. A study was also made on the residual solution, after 192 hours' boiling, and an "isomeric" cystine was isolated. The "isomeric" cystine and its derivatives were compared with the original cystine.

The data seem to warrant the following conclusions.

1. Cystine is only slowly decomposed or destroyed during long boiling with 20% hydrochloric acid. There would be no appreciable decomposition during the time of an ordinary protein hydrolysis (12-24 hours).
2. There is but little decarboxylation when cystine is boiled for 192 hours with 20% hydrochloric acid. Small amounts of carbon dioxide are evolved during the boiling.
3. The sulfur of cystine is not broken off to any appreciable extent by

boiling with 20% hydrochloric acid for 192 hours. A small amount of hydrogen sulfide is evolved, some elementary sulfur separates, no sulfates are formed, but about 90% of the original sulfur is still in an unchanged and unoxidized condition at the end of the boiling period.

4. The amount of cystine precipitated by phosphotungstic acid decreased rapidly during the first 48 hours of boiling and the amount precipitated from 48 hours until the end of the experiment remained practically constant.

5. The nitrogen of cystine was not appreciably changed during this experiment. The amount of total nitrogen remains constant, the amount of amino nitrogen slowly decreases and there is a corresponding slowly progressive increase in the amount of ammonia nitrogen.

6. The optical rotation of the cystine solution rapidly falls during the boiling period, from  $201.7^{\circ}$  to complete inactivity at the end of 96 hours.

7. An "isomeric" cystine was separated from the residual hydrolysate. This "isomeric" cystine crystallizes in small, microscopic prisms and showed markedly different behavior from the original cystine. It was approximately 2.5 times as soluble in water and the phosphotungstate was about 4 times as soluble. It showed no optical activity. The yield indicates that this compound is probably the only substance present in appreciable amounts in the residual hydrolysate.

8. This "isomeric" cystine was analyzed for its nitrogen and sulfur content and was found to be isomeric with the original cystine.

9. A number of derivatives of the two forms of cystine have been prepared and in every instance the isomeric derivatives possessed different properties from those possessed by corresponding derivatives of natural "plate" cystine. A description of the derivatives is reserved for a later communication.

10. It is suggested that the "isomeric" cystine as described in this paper is actually the cystine synthesized by Fischer and Raske, and by Erlenmeyer, and Erlenmeyer and Stoop, and that the plate cystine of protein hydrolysis has never been synthesized.

ST. PAUL, MINNESOTA.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMICAL RESEARCH, PARKE, DAVIS AND COMPANY. No. 7.]

## PYRIMIDINES FROM ALKYL MALONIC ESTERS AND AROMATIC AMIDINES.<sup>1</sup>

By ARTHUR W. DOX AND LESTER YODER.

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The condensation of dialkylmalonic esters with guanidine is well known because of its application in some of the processes for the manufacture of veronal. Aside from guanidine,<sup>2</sup> dicyanodiamide<sup>3</sup> and guanyl-urea (dicyano-diamidine)<sup>4</sup> none of the amidines appear to have been condensed with alkylmalonic esters.

In the synthesis of the malonyl-guanidines it has been assumed that the two primary amino groups of guanidine condense with the carbethoxyl groups of the malonic ester, forming substituted hexahydro-pyrimidines. It is not unlikely, however, that the tautomeric form may exist, representing a condensation in which the imino group has reacted instead of one of the amino groups, with formation of a tetrahydro-pyrimidine. The close analogy between urea, thio-urea and guanidine supports the first assumption. In the case of guanyl-urea, it is known that the condensation product is a mixture of tautomers.

Ethyl malonate has been condensed with benzamidine by Pinner.<sup>5</sup> In his first attempt Pinner obtained only the acid malonate of benzamidine. In his later work, he found that a condensation took place in the presence of aqueous alkali, but the yield was poor (10%) because of the rapid saponification of the ester. With sodium ethylate, however, the condensation occurred at ordinary temperature giving in 2 days a 50% yield of 2-phenyl-4,6-diketo-tetrahydro-pyrimidine. Pinner states that a longer time, up to 6 weeks, did not increase the yield.

Although substituted malonic esters have not been condensed with amidines, the identical products that should result from such condensations have been prepared in other ways.

Freund and Fleischer<sup>6</sup> prepared 5-5-diethyl-2-methyl-4,6-diketo-tetrahydro-pyrimidine from diethylmalonyl chloride and acetamide. From the intermediate diethylmalonyl-diacetamide first formed, the loss of acetic acid and ring closure gave the above pyrimidine. Remfry<sup>7</sup> prepared several di- and tri-alkyl-diketo-tetrahydro-pyrimidines by condensing alkylmalonamides with alkylmalonic esters. This is an unusual reaction, since the 8-membered ring expected does not form, but instead a loss

<sup>1</sup> Read at the New York meeting of the American Chemical Society, September 9, 1921.

<sup>2</sup> Fischer and Diltz, *Ann.*, **335**, 352 (1904). Gerngross, *Ber.*, **38**, 3399 (1906). Johnson and Hill, *Am. Chem. J.*, **46**, 537-49 (1911). Karst, *Ber.*, **45**, 3130 (1912). Dox and Yoder, *This Journal*, **43**, 683 (1921). Ger. pat. 189,076 (1907); 231,887 (1911); 235, 802 (1911).

<sup>3</sup> Ger. pat. 158,591 (1905); 165,223 (1905); 175,795 (1906).

<sup>4</sup> Ger. pat. 170,586 (1906); 171,147 (1906); 187,990 (1907).

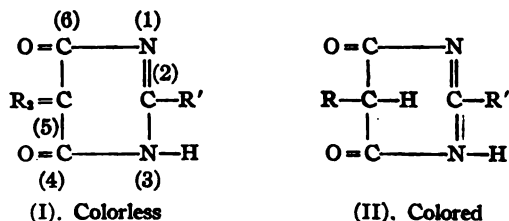
<sup>5</sup> Pinner, *Ber.*, **18**, 763 (1885); **41**, 3517-9 (1908).

<sup>6</sup> Freund and Fleischer, *Ann.*, **379**, 27-36 (1910).

<sup>7</sup> Remfry, *J. Chem. Soc.*, **99**, 610-25 (1911).

of carbon dioxide occurs and a substituted pyrimidine results. The products he obtained correspond to derivatives that should result from direct condensation of alkylmalonic esters with several aliphatic amidines. Burrows and Keane<sup>8</sup> condensed diethylmalonamide with benzaldehyde and obtained 5,5-di-ethyl-2-phenyl-4,6-diketo-hexahydro-pyrimidine. This substance would be the reduction product of the condensation product from diethylmalonic ester and benzamidine, by the simple addition of two hydrogens at the double linkage.

The experiments herein described were undertaken primarily for the purpose of studying the physiological properties of the tetrahydro-pyrimidines resulting from condensation of dialkylmalonic esters with aromatic amidines. Incidentally, it was discovered that the mono-alkyl derivatives, in contrast to the di-alkyl derivatives, are colored, suggesting a tautomeric structure. A number of the mono derivatives were therefore included among our preparations. We have then two series. Disregarding tautomeric rearrangements the formulas would be



### Experimental.

Our first experiments, in which we attempted to condense benzamidine with various dialkylmalonic esters purchased from a reliable source, caused us some perplexity. Beautifully crystalline, bright yellow, insoluble products were obtained which, however, showed the nitrogen content of the mono-alkyl instead of the expected di-alkyl derivatives. It was only when we came to work up the mother liquors that we obtained the colorless di-alkyl derivatives. In the case of ethyl dibutylmalonate we did not succeed in obtaining the dibutyl pyrimidine until after the ester had been subjected to a second alkylation with butyl bromide and sodium ethylate. In fact, of the dialkylmalonic esters purchased by us, the only one which did not give an appreciable quantity of the yellow mono-alkyl pyrimidine was ethyl dibenzylmalonate. The dialkylmalonic esters which we prepared ourselves were comparatively free from the mono derivative, yet in several instances its presence was indicated by the yellow color of the crude condensation product.

This experience recalls the observation of Fischer and Dilthey<sup>9</sup> that the esters of dialkylmalonic acids invariably contain esters of the corresponding monoalkylmalonic acids unless special precautions are taken to remove

<sup>8</sup> Burrows and Keane, *J. Chem. Soc.*, 91, 269-71 (1907).

<sup>9</sup> Fischer and Dilthey, *Ber.*, 35, 844-56 (1902).

the latter. In the case of ethyl diethylmalonate this impurity ordinarily amounts to 7-8%. The boiling points lie too closely together for a satisfactory separation by fractionation. The striking difference in the rate of amide formation when the ester is treated with aqueous ammonia is recommended by Fischer and Dilthey as a test for the presence of mono derivative and as a means of removing the latter. Meyer<sup>10</sup> showed later that this difference in the rate of amide formation is less noticeable with methyl esters than with ethyl esters, except in the case of diethyl-malonic acid. We believe that the color of the condensation product with benzamidine is an equally delicate test for the presence of monoalkylmalonic ester.

The separation of mono- from di-alkyl pyrimidines resulting from the condensation of the mixed malonic esters with aromatic amidines is, however, a simple matter. The difference in solubility is very great. The yellow mono-alkyl derivative is practically insoluble in all neutral solvents. It may be purified by dissolving in alkalies and reprecipitating it with acids, or it may be crystallized from glacial acetic acid in which it is sparingly soluble, or precipitated from this solution by dilution with water. The white di-alkyl pyrimidine, on the other hand, crystallizes readily from alcohol.

Benzamidine condenses more readily with alkyl malonic esters than does urea. For this reason, it is unnecessary, and in fact inadvisable, to use autoclave temperatures. In several experiments in which the condensations were performed at 110° the yields were very poor. A strong odor of benzonitrile was noticed, indicating a decomposition of the amidine. Our best yields were obtained at 70-75°. An excess of sodium was also found to increase the yield.

For purposes of comparison the unsubstituted malonic ester was also condensed with benzamidine, and likewise with acetamidine. Using an excess of sodium ethylate and a temperature of 105° we obtained a yield of 81% as compared with Pinner's 50% yield. The substance showed the properties of Pinner's 2-phenyl-4,6-diketo-tetrahydro-pyrimidine. We noted in addition that its behavior toward aromatic aldehydes is similar to that of barbituric and thio-barbituric acids.<sup>11</sup> In hydrochloric acid solution it immediately develops a color and finally an insoluble precipitate on the addition of an aromatic aldehyde. Benzaldehyde, cinnamic aldehyde, anisic aldehyde and piperonal all gave derivatives whose color varied from yellow to brick-red. These precipitates were soluble in alkalies, but insoluble in all other solvents and difficult to obtain sufficiently pure for analysis. In acetic acid solution no reaction occurs until a few drops of hydrochloric acid are added.

<sup>10</sup> Meyer, *Ber.*, 39, 198-200 (1906).

<sup>11</sup> Dox and Plaisance, *THIS JOURNAL*, 38, 2164-6 (1916).



The procedure followed in the preparation of the alkyl substituted pyrimidines was in the main the same throughout; hence a single protocol for each series will suffice by way of illustration. The amidines were prepared from the respective nitriles through the imido-ether salts.

**5,5-Diethyl-2-phenyl-4,6-diketo-tetrahydro-pyrimidine.**—To a solution of 4.5 g. of sodium in 75 cc. of absolute alcohol, 9 g. of benzamidine hydrochloride and 10 g. of carefully purified ethyl diethylmalonate were added. The mixture was heated for 7 hours at 70°. The alcohol was partially removed by a current of dry air and the residue acidified with a slight excess of conc. hydrochloric acid. After removal of the precipitated sodium chloride, the solution was further concentrated on the steam-bath. The addition of water caused the product to separate in white needles. The yield was 5 g. The substance was recrystallized from dil. acetic acid. It will be noted in this instance that the yellow color due to the formation of mono-alkyl derivative was not observed. This we attribute to the fact that the ethyl diethylmalonate had been given a second treatment with ethyl bromide and sodium ethylate, and the usual impurity of ethyl monoethylmalonate was not present.

**5-Benzyl-2-phenyl-4,6-diketo-tetrahydro-pyrimidine.**—To a solution of 1.5 g. of sodium in 20 cc. of absolute alcohol, 2.8 g. of benzamidine

TABLE I

## 4,6-DIKETO-TETRAHYDRO-PYRIMIDINES

Nos. 1-4 and 14-21 were white; the others were yellow in color

	Substituents		Melting point °C.	Calc. %	Nitrogen Found		Yield %
	5-carbon	2-carbon			%	%	
1.	.....	methyl	300+	22.22	22.08	22.15	62
2.	phenyl	methyl	300+	13.86	13.45	13.31	70
3.	benzyl	methyl	300+	12.96	12.70	12.91	85
4.	.....	phenyl	300+	14.89	14.43	14.63	81
5.	methyl	phenyl	300+	13.86	13.57	13.65	..
6.	ethyl	phenyl	300+	12.96	12.92	12.78	..
7.	allyl	phenyl	288-9	12.28	12.27	12.34	70
8.	butyl	phenyl	296-7	11.47	11.34	11.41	44
9.	isoamyl	phenyl	300+	10.85	10.71	10.99	45
10.	benzyl	phenyl	300+	10.07	10.01	9.87	100
11.	dimethyl	phenyl	263	12.28	12.39	12.53	61
12.	ethyl	p-tolyl	300+	12.17	11.88	12.23	..
13.	ethyl	p-ethoxy-phenyl	300+	11.47	11.31	11.15	..
14.	dimethyl	phenyl	184	12.96	12.71	12.64	45
15.	di-ethyl	phenyl	207	11.47	11.37	11.49	44
16.	dipropyl	phenyl	164	10.29	10.47	10.19	45
17.	dibutyl	phenyl	144	9.33	9.27	9.41	..
18.	dibenzyl	phenyl	234	7.61	7.40	7.62	37
19.	di-ethyl	p-tolyl	181	10.85	10.80	10.88	40
20.	di-ethyl	p-ethoxy-phenyl	165	9.75	9.73	9.65	..
21.	di-ethyl	β-naphthyl	178	9.52	9.45	9.59	59

hydrochloride and 4 g. of ethyl benzylmalonate were added. The mixture was kept at about 40° for 12 hours. It was then acidified with conc. hydrochloric acid, the yellow precipitate collected on a filter and the sodium chloride washed out with water. The crude product weighed 4.5 g. It was insoluble in water and the neutral organic solvents. It dissolved with difficulty in glacial acetic acid from which it was obtained as bright yellow needles on cooling the solution. In mineral acids and alkalies it dissolved to give a colorless solution from which the yellow crystals were again obtained on neutralization.

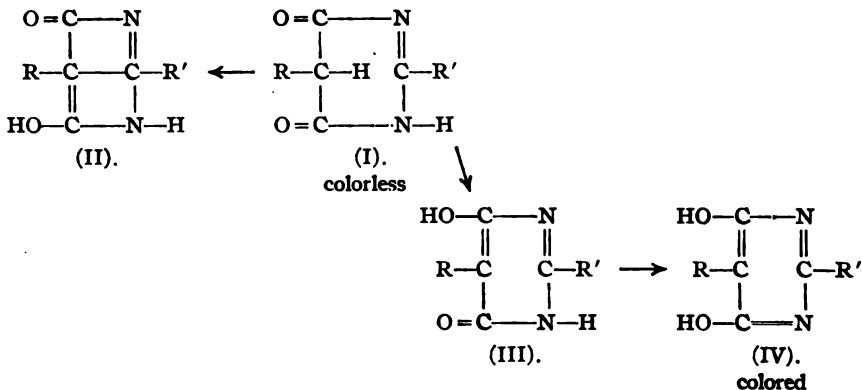
The two series of derivatives which we prepared from mono- and dialkylmalonic esters are listed in the preceding table. In the case of 5-mono-alkyl derivatives where the yield is not stated, the substance was obtained as a by-product accompanying the corresponding di-alkyl derivative.

#### Discussion.

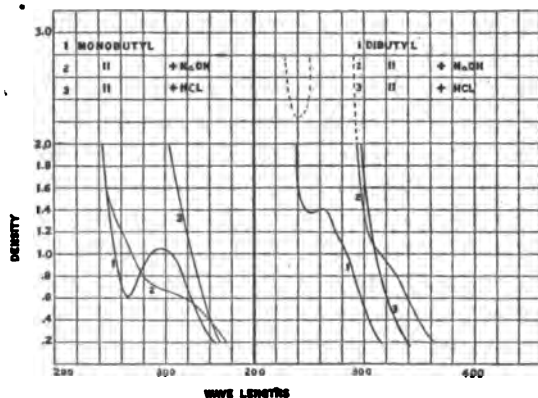
In the foregoing table several pairs of isomers will be noted, of which one is colorless and the other colored. In Nos. 2 and 5 the positions of the methyl and phenyl are simply reversed. Nos. 8 and 15 show isomerism due to an alkyl group in one case, equivalent to two smaller alkyl groups in the other. Nos. 9 and 19 are analogous to the preceding with the additional variation of a methyl group attached in the one case to the 5-alkyl group, and in the other to the 2-aryl.

It will be noted that the 5-mono-alkyl derivatives from the aromatic amidines are all yellow, and with two exceptions do not melt below 300°. Pinner states that his 5-bromo-2-phenyl-4,6-dioxy-pyrimidine was bright yellow in color and melted with decomposition at 320°. Evidently a halogen on the 5-carbon atom is equivalent to an alkyl group. The 5,5-di-alkyl derivatives, on the other hand, are all colorless and melt considerably below 300°. An apparent exception to the color rule is the trimethylene derivative which, however, is a *spiro* compound. The difference in solubility has already been pointed out. The presence of the 2-aryl group appears to be necessary for the manifestation of color in the 5-mono-alkyl series, since corresponding derivatives with methyl in place of the aryl group are colorless. Leaving out of consideration the *spiro* derivative (No. 11), the two criteria which determine color in the 4,6-dioxy-pyrimidines are a 2-aryl group and a 5-hydrogen atom. The latter makes possible a rearrangement into a tautomeric enolic form with 3 double linkages in the ring.

A hemiquinoid structure (Formula II) does not in itself imply color. Such structure is known where color is absent. Formula III does not account for the color, since a similar structure with 2 alternate double linkages can also be assigned to the 5,5-di-alkyl derivatives which are invariably colorless. Formula IV, therefore, represents the most probable



structure of the colored derivatives. Through the kindness of Dr. H. T. Clarke, of the Eastman Kodak Company, the absorption spectra of typical yellow and colorless derivatives were determined by means of the spectrophotometer. The curves below, where density of absorption is plotted against wave length, were obtained by using a 1cm. layer of 0.00005 *M* solutions in methyl alcohol. The monobutyl derivative shows a decided band (Curve I) in the violet, which disappears on the addition of a few



drops of alkali or acid (Curves II and III). The dibutyl derivative shows only an extension in the region beyond the visible. The effect of alkali in this case is to produce a band corresponding in position to the extension shown by the pure substance. With both derivatives the effect of acid is a strong general absorption nearer to the visible.

### Summary.

Alkylmalonic esters condense readily with aromatic amidines, the monoalkylmalonic esters yielding insoluble yellow pyrimidine derivatives, and the dialkylmalonic esters soluble, colorless derivatives. The color may perhaps be explained on the basis of tautomeric rearrangement.

DETROIT, MICHIGAN.

[CONTRIBUTION FROM THE ORGANIC LABORATORY OF THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY.]

## THE CONSTITUTION OF THE SECONDARY PRODUCT IN THE SULFONATION OF CINNAMIC ACID.

By F. J. MOORE AND RUTH THOMAS.

Received September 21, 1921.

Cinnamic acid, when treated with fuming sulfuric acid, yields 2 sulfonic acids, the more abundant being the *para* derivative. Rudnew,<sup>1</sup> who first carried out this reaction, believed the other product to be a *meta* compound because, on fusion with potash, it yielded *m*-hydroxybenzoic acid. Beilstein,<sup>2</sup> however, questions this conclusion, and points out (1) the frequent rearrangements which take place in a potash fusion, (2) the uniformity with which *ortho* and *para* compounds are simultaneously formed, and (3) the fact that Kafka<sup>3</sup> had already prepared a *meta* acid from *m*-sulfobenzaldehyde by the Perkin synthesis, which leaves hardly a doubt as to the constitution of the product. Doubtless for these reasons Richter's "Lexikon" describes the acid of Kafka as *meta* and the secondary product of Rudnew as *ortho*, in spite of the fact that Kafka's description contains no criteria by which his acid could be distinguished from the other, and that Palmer,<sup>4</sup> who had oxidized the amide of the latter in the expectation of obtaining "saccharine," was not successful—an argument against the *ortho* position.

The present work shows that the secondary product of sulfonation is a *meta* compound because permanganate transforms it smoothly to *m*-sulfobenzoic acid. It is also identical with the acid of Kafka which has been prepared for comparison.

### Experimental.

In a study of the *para* acid made by one of us<sup>5</sup> some years ago, several grams of the acid barium salt of the *meta* acid had accumulated, and this material furnished the starting point for the present investigation. The salt is a good deal more soluble in water than is the *para* compound and crystallizes in warty aggregates, very different from the long beautiful needles which characterize the *para* salt.

***m*-Sulfobenzoic Acid.**—Five g. of this salt was converted into the potassium salt by boiling it with a concentrated solution of 2.5 g. of potassium carbonate. Then 7.2 g. of potassium permanganate was stirred into the warm filtered solution. Oxidation was immediate. After the addition of a little alcohol the solution was filtered from manganese dioxide and evaporated to dryness. The *m*-sulfobenzoic acid which it contained was not isolated as such, but was identified by the following derivatives.

<sup>1</sup> Rudnew, *Ann.*, 173, 8 (1874).

<sup>2</sup> Beilstein, "Handbuch d. org. Chem.," 3rd ed., vol. II, p. 1422.

<sup>3</sup> Kafka, *Ber.*, 24, 796 (1891).

<sup>4</sup> Palmer, *Am. Chem. J.*, 4, 161 (1882).

<sup>5</sup> Moore, *THIS JOURNAL*, 25, 622 (1903).

***m*-Sulfobenzamide.**—Seven-tenths g. of the residue (containing much potassium carbonate) was heated with 2 g. of phosphorus pentachloride in a small distilling flask, at first on the water-bath and then to about 150°, to remove phosphorus oxychloride. The product, when treated with ice-water, yielded about 1 cc. of a heavy oil. This was added drop by drop to ammonium hydroxide (sp. gr., 0.90). After the product cooled, it was washed with water, dried on a porous tile, and recrystallized from absolute alcohol. It melted at 171–172°, and a mixture of it with *m*-sulfobenzamide prepared from another source melted at the same temperature.

***m*-Hydroxybenzoic Acid.**—To obtain this acid, 1.72 g. of the same residue was fused with 15 g. of potassium hydroxide and a little water at 220–240° for 45 minutes. The melt was dissolved in water, just acidified with hydrochloric acid and extracted thrice with ether. The combined extracts yielded 0.55 g. of a crusty residue. Four crystallizations from water yielded a product melting at 200–201°, and a mixture of this product with *m*-sulfobenzamide from another source melted at the same temperature. Both gave an unmistakable (dirty) brown coloration with ferric chloride which confirms the experience of Velden,<sup>6</sup> although most books state that this acid gives no color with ferric chloride.

**Acetyl Derivative.**—For further identification, the acid was transformed into its acetyl derivative according to the directions of Heinz<sup>7</sup> and a product with the melting point recorded by him (127°) was obtained.

***m*-Sulfobenzaldehyde.**—This substance, which is the necessary starting point in the synthesis of Kafka, had been prepared by Wallach and Wüsten.<sup>8</sup> They do not state the strength of their sulfuric acid, but we found that any acid containing less than 40% of anhydride was inefficient, and even with this strength it was necessary to warm the mixture for several hours on the water-bath before all the benzaldehyde was sulfonated. From the reaction mixture the barium salt was obtained in the customary way and a barium determination (calc., 27.16%; found, 26.35%) showed that sulfonation had not passed beyond the introduction of one sulfo group.

***m*-Sulfocinnamic Acid.**—Kafka heated the barium salt of *m*-sulfobenzaldehyde with sodium acetate and acetic anhydride. The product was acidified with sulfuric acid and distilled with steam to remove acetic acid. It was then evaporated to dryness and the residue extracted with alcohol. We found it impracticable to remove the large quantities of acetic acid with steam satisfactorily, and obtained only poor yields of impure material in this way. Better results (still far from good) were obtained as follows.

Ten g. of the barium salt of *m*-sulfobenzaldehyde was intimately ground with 5 g. of freshly fused sodium acetate and the mixture treated with 22 cc. of acetic anhydride. The whole was then boiled for 13 hours. After cooling the mixture, it was treated directly with ether to remove as much acetic anhydride as possible at this point. The portion insoluble in ether was dissolved in water and precipitated by sodium carbonate. The filtrate from barium carbonate was then evaporated to dryness. The residue should contain the sodium salt of sulfocinnamic acid along with considerable acetate and carbonate. It was proposed to transform the acetate and sulfonate to the acid chlorides and separate them by the greater sensitiveness of acetyl chloride to water. The original residue had weighed 31 g. Fifteen g. of it was treated with 30 g. of phosphorus pentachloride in the cold and after half an hour the mixture was poured upon ice. When the material soluble in water had been removed, the waxy residue was boiled with water to transform the acid chloride into the free sulfonic acid. The product was a greasy solid unsuitable for analysis (Kafka did not analyze it),

<sup>6</sup> Velden, *J. prakt. Chem.*, [2] 15, 165 (1877).

<sup>7</sup> Heinz, *Ann.*, 153, 338 (1870).

<sup>8</sup> Wallach and Wüsten, *Ber.*, 16, 150 (1883).

but was identified by transformation into the acid barium salt which crystallized in the warty aggregates already described, and by the preparation and analysis of the acid aniline salt.

**ANILINE SALT.**—Like Palmer, we found it difficult to prepare a homogeneous amide of *m*-sulfocinnamic acid, but one of us<sup>4</sup> had already pointed out that it is frequently more convenient to characterize sulfonic acids by their salts with organic bases. This proved to be the case here. A solution of the crude acid in 5 times its weight of water was mixed with its own weight of aniline sulfate in suspension. The mixture solidified at once. It was warmed until solution was complete and then cooled. The product obtained was dried and crystallized 4 times from a mixture of alcohol and ether, from which it separated in lustrous needles melting at 238° with evolution of gas.

**Analyses:** Subs., 0.4123: 15.2 cc. N, (20°, 744 mm.). Subs., 0.1603, 0.1574: BaSO<sub>4</sub>, 0.1174, 0.1153. Calc. for C<sub>14</sub>H<sub>11</sub>O<sub>3</sub>NS: N, 4.36; S, 9.97. Found: N, 4.28; S, 10.00, 10.06.

The identity of this compound with the acid aniline salt of the acid formed by sulfonating cinnamic acid was established by preparing the salt from that source for comparison. It was found to contain 4.26% of nitrogen and melted at 238°. A mixture of the 2 samples melted at the same temperature.

A *p*-toluidine salt of the acid made by sulfonation was also prepared. It was more difficult to purify and was not analyzed. It melted at 229–230° with gas evolution.

### Summary.

1. The secondary product formed in the sulfonation of cinnamic acid is *m*-sulfocinnamic acid. It is identical with that already obtained from *m*-sulfobenzaldehyde by the Perkin synthesis.

2. The *ortho* acid is therefore still unknown. Attempts are in progress to prepare it, and to make a comparative study of the three.

3. Another case has been found which illustrates the convenience of characterizing sulfonic acids by their salts with organic bases.

CAMBRIDGE 39, MASSACHUSETTS.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE NEW YORK STATE HOSPITALS.]

## IDENTIFICATION OF ALKALOIDS UNDER THE MICROSCOPE FROM THE FORM OF THEIR PICRATE CRYSTALS.

BY BURT E. NELSON AND HELEN A. LEONARD.

Received September 26, 1921.

No satisfactory systematic scheme for the qualitative identification of all the common vegetable alkaloids is known, and while certain partial schemes serve fairly well for particular groups, they frequently do so only in the known absence of others. Moreover, many of these schemes and in fact the classical methods for identifying organic compounds generally, are quite frequently inapplicable because of the small amount of material available, particularly in the analyses of certain medicines and in forensic cases. The well-known color reactions, often interpreted largely by a

process of exclusion, while applicable to small portions of residues, have the disadvantage of destroying the material for further tests.

Micro-chemical and micro-crystallographic methods (the latter including determinations of refractive indices) have here the distinct advantages of utilizing only a small amount of material, and often of leaving the alkaloid in a combination suitable directly for melting-point determinations and from which it may be again obtained in free form for color reactions, pharmacological tests, etc.

Among the compounds utilized most frequently for micro-chemical identification of alkaloids the picrates have long been popular, although in many instances the picrolonates serve better. Other commonly used double compounds are those with gold and platinum chlorides, iodo-potassic, iodo-mercuric, bismuthic and cadmic iodides, etc.

In using these compounds we have felt the need of a convenient reference chart for quickly classifying into crystal groups and arriving at the probable base or bases present from the form or "habit" of the crystals, or at any rate for determining the base to be probably one of a few, before proceeding to further crystallographic or chemical tests for the final identification. For this preliminary comparison it is obviously necessary to use the same derivative of the alkaloids, and for our own use the picrates were chosen because they can as a rule be conveniently precipitated directly from many mixtures and because their forms are usually quite diverse and characteristic. For the further confirmatory tests, however, they are less suitable than the common acid salts and some double compounds, because their high refractive indices preclude the possibility of determining these values by the immersion method with any of the liquids now used.

The figures in the accompanying chart, however, have to do only with the form or habit of the crystals, and this we have found to be constant after following the procedure given below. Thus far we have not found that the presence of another alkaloid offers serious interference. The chart has, in fact, in many cases been useful even without subsequent confirmatory optical tests, although naturally these should be made.

All of the alkaloids studied met the pharmacopeial requirements. Aconitine was of the amorphous active variety. Caffeine and theobromine among the purin bodies, and free picric acid, are included for comparison, in the drawings.

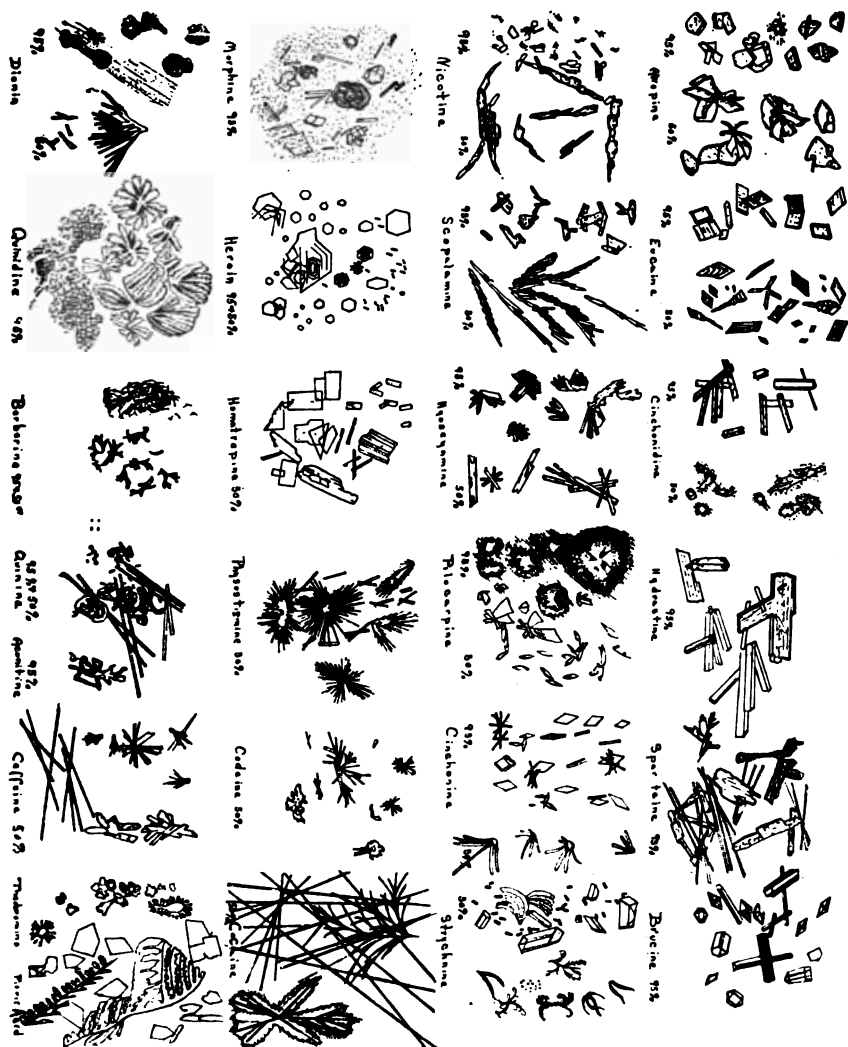
In using the form or habit of the picrate crystals for this preliminary identification, it must not be forgotten that except when obtained under identical physical conditions form is not a fixed and unchanging physical property. Among the conditions influencing the form may be mentioned temperature, concentration and purity of the solution crystallized, and the rate of crystallization. Even the presence of traces of grease on the micro-

scope slides will often affect the result. Where crystallization occurs from too dilute a solution or over too large a cell area, "starved" or skeleton crystals are apt to form in feathery or fern-like dendritic masses.

For the above reasons uniform methods of procedure must be followed, and after the first examination it is well to repeat the crystallization and to compare with a known standard similarly treated to insure constant results.

### Method.

The aqueous solution (fairly concentrated in a few cases) of the separated alkaloid, slightly acidified with hydrochloric acid, is precipitated in a





small test-tube with a slight excess of saturated solution of picric acid and the precipitate deposited and slightly washed in a centrifuge. The picrates are now dissolved in a corked test-tube in the smallest practical volume of warm 95% alcohol, the tube being held in a warm water-bath. The solution is next allowed to cool somewhat slowly with the bath, when crystals will usually form. Further strong cooling will increase the yield. The crystals are now deposited firmly in the centrifuge and the supernatant fluid decanted as completely as possible into a second small test-tube. By means of a curved, pointed glass rod the crystals are now transferred, together with any adherent mother liquor to a paraffin-ringed cell on a glass microscope slide. This cell is conveniently made by touching the warmed smooth-cut end of a thin metal tube, first to a solid block of paraffin and then squarely against the glass. An equal volume of water is next added to the remaining alcoholic solution in the second tube, previously concentrated if necessary, so that on adding to the remaining crystals in the first tube the former are again dissolved completely only on warming, and a second lot of crystals obtained as above with this 50% alcoholic solution. The whole operation will not, as a rule, require more than 10 or 15 minutes.

In this manner we obtain 2 separate cells of crystals, from one or both of which characteristic forms will usually be obtained. These are to be compared with the figures and the known sample similarly treated.

Direct addition of the reagent to an acidified drop of solution on the microscope slide has not furnished as reliable results with us.

For this tentative identification of the crystals thus formed only an ordinary microscope is, of course, required, but for optical crystallographic measurements, which are nearly as applicable to powder fragments as to entire crystals, a good petrographic or chemical microscope is essential. As the present article does not consider the methods of optical crystallography or chemical microscopy, the beginner is referred to standard texts,<sup>1</sup> although we hope to present the crystallographic data later.

In the mean time this preliminary but tentative identification by means of the chart will, we trust, be convenient.

<sup>1</sup> Parker, "Some Microchemical tests for Alkaloids," J. B. Lippincott Co. Chamot, "Elementary Chemical Microscopy," John Wiley and Sons Co. Luquer, "Minerals in Rock Sections," John Wiley and Sons Co. McCoughey and Fry, "The Microscopic Determination of Soil Forming Minerals," *Bull.*, 91, U. S. Dept. Agriculture. Wherry, "The Application of Optical Methods of Identification to Alkaloids and Other Organic Compounds," *Bull.*, 679, U. S. Dept. Agriculture. Groth, "Elemente der physikalischen und chemischen Krystallographie," R. Oldenbourg, Berlin. Wright, "The Petrographic Microscope in Analysis," *THIS JOURNAL*, 38, 1647 (1916). Wormley, "Microchemistry of Poisons," J. B. Lippincott Co. Behrens, "Anleitung zur mikrochemischen Analyse," Wherry and Yanovsky, "The Identification of The Cinchona Alkaloids by Optical-Crystallographic Methods," *THIS JOURNAL*, 40, 1063 (1918).

### Summary.

We believe that the more commonly occurring vegetable alkaloids may be tentatively identified under the microscope by the form or habit of their picrate crystals prepared under standard conditions. We hope to consider the optical properties of other of their compounds later.

BINGHAMTON, NEW YORK.

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[COMMUNICATION No. 131 FROM THE RESEARCH LABORATORY OF THE EASTMAN KODAK COMPANY.]

## THE DRYING AND SWELLING OF GELATIN. PRELIMINARY NOTE.<sup>1</sup>

By S. E. SHEPPARD AND F. A. ELLIOTT.

Received October 27, 1921.

The following notes, or more accurately notes and queries, are concerned principally with the influence of the earlier phases of a dehydration-hydration cycle in gelatin jellies on later phases of the cycle. The view that the influence of the history of a gelatin gel on its swelling after drying is explicable in terms of an internal supermolecular structure has been recently clearly expressed by L. Meunier. In a review of recent work "On the Properties of Gelatin"<sup>2</sup> he states "We have already mentioned that according to Hardy's conception, the solid phase of a gelatin jelly has a structure related to its concentration; the cells of the lattice would be open in the case of the less concentrated jellies, and closed in the case of the more concentrated. Admitting this hypothesis, it may be conceived that the absorbing power for water of thin sheets of gelatin will be in relation to the concentrations of the solutions from which they are prepared. If we prepare from the same gelatin two solutions, one at 6%, the other at 20%, and coat thin sheets of gelatin from these on glass, dry at low temperature, the leaves prepared from the diluted solution will absorb more water and will swell more, for equal weight [of gelatin] and time, than the sheets prepared from the concentrated solution."

Similar experiments are recorded by H. R. Procter<sup>3</sup> and by W. D. Bancroft<sup>4</sup> and have been confirmed in this Laboratory. There remains the question as to whether they are due to internal structure, as suggested, or whether a more obvious cause exists.

### The Drying of Gelatin Jellies.

Gelatin jellies, of given definite geometrical shape and water content, might be supposed to dry in such a way that the shape would remain un-

<sup>1</sup> Paper read at the Spring Meeting of the American Chemical Society, Rochester, N. Y., April, 1921.

<sup>2</sup> Meunier, *Chimie et industrie*, 5, (T.) 220 (1921).

<sup>3</sup> Procter, *J. Chem. Soc.*, 105, 313 (1914).

<sup>4</sup> Bancroft, "Applied Colloid Chemistry," McGraw-Hill Book Co., 1921, p. 251.

affected. Such shrinkage, and a swelling exactly inverse thereto, we may term isometric; actually isometric shrinkage of jellies on drying can be approached only by very slow drying under conditions such that the environment is only slightly unsaturated as to water or water vapor. Ordinarily this is not the case; hence, the rate of diffusion of water to the drying surface is not everywhere the same and equal to the rate of evaporation. The importance of diffusion in regulating the drying and swelling of gelatin masses has been pointed out by (Miss) E. B. Shreve,<sup>5</sup> whose work will be referred to subsequently. The actual balance between the diffusion in the gel and the surface evaporation is affected by a number of factors as follows.

1. **Environment factors.**—*i. e.*, the saturation, temperature, rate of movement of the dehydrating fluid, *e. g.*, air.

2. **Surface factors.**—The surface is not a geometrical boundary of negligible thickness and structure, but a region of discontinuity of physical properties and state of aggregation. If we term the sum total of the surface energy factors the *capillarity*, this becomes of still more pronounced and even critical importance at the intersection of geometrical surfaces, such as edges and corners (dihedral and polyhedral angles).

3. **Elastic factors.**—Although a gelatin jelly is a relatively homogeneous isotropic solid for simple shearing stresses not involving compressions or dilations,<sup>6</sup> it tends to become heterogeneous and aeolotropic for complex stresses such as occur in drying and swelling. This, again reacts on the progress of drying and the properties of the piece of gelatin.

4. **Associated factors.**—Temperature, pressure and chemical conditions are variables associated with both the superficial and the elastic variables; these, as independent variables, define the limits within which gelatin solutions behave as elastic hydrogels. If the temperature and pressure are above certain values, equilibrium is definitely displaced in the direction of the sol condition, in which the rigidity is negligibly small compared with the resistance to compression (bulk elasticity). Again at constant temperature, the chemical potentials, in particular, the hydrogen-ion concentration, definitely limit the concentration region of gel formation. An originally uniform distribution of a chemical potential can readily become nonuniform, again with a definite reaction on the progress of drying and the properties of the dried piece.

Passing from these preliminary generalities, we note the behavior of gelatin in various forms on ordinary "forced" drying and subsequent swelling.

#### Leaf Gelatin.

Preparation in "leaf" form is very usual for technical and photographic

<sup>5</sup> Shreve, *Science*, 48, 324 (1918).

<sup>6</sup> Sheppard and Sweet, *THIS JOURNAL*, 43, 539 (1921).

gelatin. The shape and behavior on swelling, for a given stock, are primarily determined by the concentration and thickness at which it was "set," by the fact that it is dried down on a net or mesh, and by the rate of drying. Such a leaf shows in a polariscope local strain areas about the nodes of the net, and evident thickenings at the traces of these nodes and the mesh work on the leaf, as also at the edges. Between the meshlines the gelatin is thinner and has a curved surface. The behavior on swelling is illustrated by the following data.

EXPT. 1					
Dimension	Swelling			Swelling	
	0 hrs.	1.5 hrs.	$\frac{ds}{s}$ %	18 hrs.	$\frac{ds}{s}$ %
Length	23.1 cm.	24.3 cm.	5.2	28.2 cm.	22.2
Breadth	8.5 cm.	9.7 cm.	14.1	10.3 cm.	21.2
(a) Center					
	mesh	0.108	0.83	670.0	1.09 910
Thickness in cm.	(b) Nodes	0.70	0.90	14	1.10 50
	(c) Edges	0.45	0.90	100	
EXPT. 2					
Dimension	Swelling			Swelling	
	0 hrs.	1.5 hrs.	$\frac{ds}{s}$ %	18 hrs.	$\frac{ds}{s}$ %
Length	22.7 cm.	25.5	12.3	27.5 cm.	21.1
Breadth	8.6	9.0	4.65	10.2	18.6
(a) Center					
	mesh	0.142	0.82	0.477	1.22 760
Thickness in cm.	(b) Node	0.75-.80			1.22 50
	(c) Edges	0.55			1.3
Weight, g.	3.790	20.89	450%	34.46 g.	810%

It will be seen from these that the dilations in length and breadth are very small, compared with the dilation of the thickness of the intermesh elements; this increase in thickness is alone nearly able to take care of the total increase in volume as may be seen by comparing the parallel figures for the increase in weight. It is evident that these results approach the behavior of gelatin jelly coated and dried down on a glass plate, when on swelling the dilation is necessarily confined to the direction perpendicular to the plane of the plate, frilling and stripping excluded. The similar behavior of leaf gelatin is due to similarity of cause. The meshwork of the supporting net initiates the drying by capillarity and thus the sheet receives a skeleton or framework of primarily hardened, rigid gelatin, evident enough upon examination, which is simply a capillary impress of the net. This framework, consisting of more compact gel, is composed of the nodal bosses or cusps (somewhat thicker, as will be seen from the measurements, than the intermesh elements), the internodal

lines of the mesh, and the edges, also thicker. The intermesh elements are curved away from the plane of the mesh, and the flattening out of the curvature on swelling probably plays a considerable part in the approximate re-formation of the original trapezoidal sheet form. On redrying, freely suspended, the sheet is approximately reshrunk to the original leaf form, the intermesh elements going back to their former thickness. This unilateral dilation of the leaf is not peculiar to the leaf as a whole, but is shared by pieces cut out of the intermesh elements, *e. g.*, with a cork borer. Thus, after 3 hours 1.1 cm. diameter became 1.5 cm. ( $ds/s$  36%) and 0.10 mm. thickness became 1.05 mm. ( $ds/s$ , 950%).

This was observed by R. Cahal also, in the course of his researches on the microscopic structure of Lippmann images, by microtome sections through gelatin films stripped from a photographic plate. Cahal in order to magnify the distance between the elemental mirrors, employed the device of swelling the section in water, and noticed that the section swelled some 10 times in the direction of the normal to the plane of the plate and but little in the transverse direction. This has been corroborated in this Laboratory.

Initiation of an external skeleton framework, which acts similarly to an adherent plate or film support, appears sufficient to explain the unilateral swelling of a sheet of dried down gelatin as a whole, while the like behavior of pieces and sections indicates that the distribution of strain effected in drying extends to microscopic and perhaps submicroscopic elements. Since the capillary initiation or induction appeared to be a phenomenon of fundamental importance for the drying and swelling of gelatin, experimental attention was directed to reducing this factor progressively as far as possible. If we pass successively from *cubes* to *cylinders* to *spheres*, we have a progressive reduction of the corner and edge factors to zero, and arrive at a figure for which the ratio of surface to volume is a minimum. Experiments were made with such figures, with various modifications of procedure.

**Cubes.**—Three cases were observed: (a) cube freely suspended, all faces free, (b) cube bounded at one face; (c) cube bounded at two opposite faces. The cubes were cast in special moulds, with a removable suspension consisting of a rigid wire terminated by a small cubical block acting as the center of the cast piece. The relatively slight capillary action of the wire can be reduced by greasing it. The cubes were made in three sizes: 2.5 cm. = 1.0 inch (No. 3), 1.25 cm. = 0.50 inch (No. 2) and 0.62 cm. = 0.25 inch (No. 1). While geometrical similarity induced a similar behavior on drying in the three cubes, the process was the more rapid the smaller the cube. Experiments were made both with dynamic drying (air current) and statically (in a closed vessel) over sulfuric acid of definite concentration. The general results were the same in both cases, but

experiments are being continued over a wider range of condition as to speed, temperature and saturation of the air.<sup>7</sup> The actual progress of drying will be most readily seen from the photographs (Fig. 1).

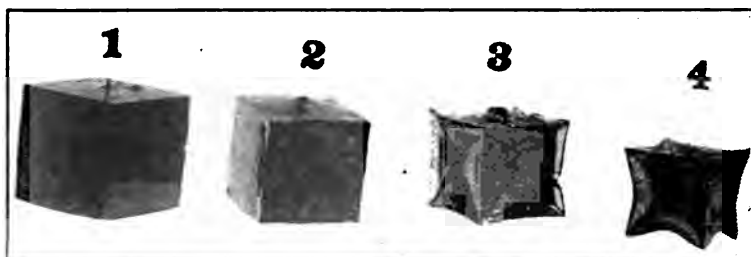


Fig. 1.—Free cube.

1—Original 20% gelatine; 2—Initial drying step; 3—Intermediate; 4— Final drying.

These are for 20 % gelatin jellies. It is evident that drying is *initiated* at the corners or trihedral angles which dry and harden first; at this stage the sides or faces of the cube are bowed or curved outward, giving convex surfaces under tension. This is rapidly followed by hardening of the edges, which tends to flatten the faces again. A rigid framework is thus formed, so that the cube behaves as if suspended inside a relatively unyielding wire cage. The faces now recede, and the edges become somewhat incurved till a sort of inner cube is formed with connected flanges reinforcing it, any cross-section through this having an I-beam structure, as though the drying proceeded in a manner developing the figure with the greatest resistance to stress. The flange-like edges appear to form sections of hyperboloids with a common focus at the center of the cube.

When one face is bounded, as by standing the cube on a sheet of glass, the only noticeable difference is that drying starts at the intersection of the cube with this base. Hence the basal face persists practically unaltered in size. This is duplicated in the case of two parallel faces being bounded when the effect of capillarity at the contact angles in directing the drying becomes still more marked (Fig. 2).

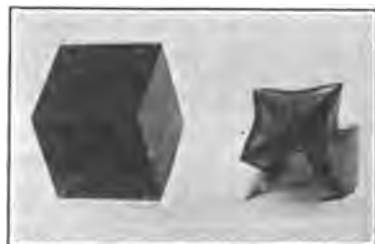


Fig. 2.

Cubes, 1—Face suppression before and after drying 1 inch.

On placing such a cube in water and allowing it to swell, at first the

<sup>7</sup> By very slow drying we have secured isometric shrinkage, and investigation of swelling inverse to this is in progress.

salients formed tend to swell most; this is then followed by restitution of the faces, and an approximate restoration of the original cube. The course of drying—up to about 6 to 10% moisture content—as described, has increased the ratio of surface to volume. If a freshly moulded cube of some 60% gelatin is placed in water, swelling also starts at the corners and edges, producing the same type of deformation. Quincke has observed that a cube or sphere of jelly on drying shows by polarized light negative double refraction in the outer shell and positive double refraction in the interior, the optic axis being normal to the surface; on swelling these conditions are reversed, showing a reversal of the distribution of stress.

Passing from the case of a cube with one face bounded, we may consider any right 6-face, with one bounded (or suppressed) and the *thickness*, taken perpendicular to this face, small compared to the other dimensions. In the limit this corresponds to photographic plates and films. In this case drying proceeds very similarly at first to the cube, but the sides soon become incurved and case-hardened, so that in the second stage drying proceeds by gradual envelopment and reduction in area of a central humid zone, proceeding inward from the corners and edges.

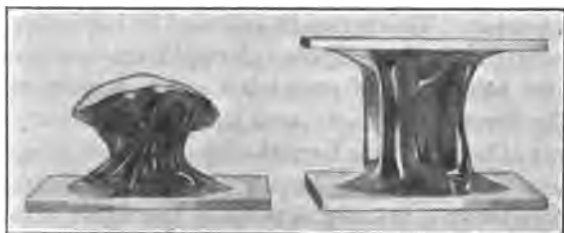


Fig. 3.  
Cylinders, 1—Face, and 2—Face suppression after drying,  
side view.

In the case of cylinders and spheres, the photographs show that shrinkage on drying is not uniform, but produces a puckered or wrinkled surface (Fig. 3).

#### Case Hardening vs. Structure.

Our conclusion is that the "case hardening" effect, in particular as initiated at edges and corners, is responsible for two important phenomena in the hydration-dehydration cycle of gelatin jellies. The first of these is the fact noted in reference to "leaf" gelatin, and pointed out by Miss E. B. Shreve<sup>6</sup> "that the greatest shrinkage and subsequent swelling takes place perpendicular to the largest evaporating surface." The second is the apparent influence of the original concentration of the gelatin jelly on its swelling limit subsequent to drying. This we regard as being due to the initial case-hardening, which preserves an approximate "skin

extension" corresponding to the original figure. If this is correct, there appears no need to postulate an internal sub-microscopic but super-molecular structure of the gelatin. Any "structure" is not inherent in the gelatin, but is an environment impress, a strain structure in the original mass.<sup>8</sup> We are continuing the investigation of this with controlled humidity, to adjust the rate of evaporation.

The influence of hydrogen-ion concentration on swelling of gelatin masses with different drying histories is also under investigation, in relation to the Procter-Wilson-Loeb theory of gelatin swelling.<sup>9</sup>

ROCHESTER, NEW YORK.

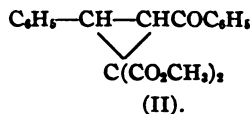
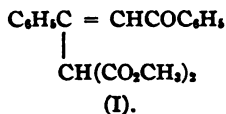
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY.]

## THE ADDITION OF MALONIC ESTERS TO BENZOYL-PHENYLACETYLENE.

By E. P. KOHLER.

Received October 28, 1921.

The following investigation was originally undertaken for the purpose of making the unsaturated  $\delta$ -ketonic acid (I) for comparison with an isomeric cyclopropane derivative (II).



It was abandoned for a time because the addition reaction gave substances of a different type, and then taken up again in the hope of finding

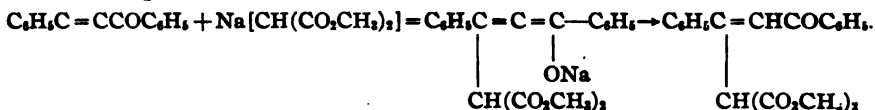
<sup>8</sup> This view may be compatible with a development of the 2-phase theory for gelatin gels, with the proviso, however, that the structure elements are resultants of the physico-chemical changes of environment, not native to gelatin. Thus Miss J. Lloyd (*Biochem. J.*, 14, 166 (1920)) pictures gelation as follows: "gelation will only occur on the cooling of a sol which contains in solution iso-electric gelatin and gelatin salts in equilibrium with free electrolytes. As the sol is cooled the insoluble iso-electric gelatin is precipitated in a state of suspended crystallization and forms a solid framework throughout the system. The more soluble gelatin salts remain in solution and by their osmotic pressure keep the framework extended. Gels, therefore, are 2-phase systems, the solid phase consisting of iso-electric gelatin, the liquid of gelatin in salt form." With regard to this conception, if the insoluble iso-electric gelatin forms a rigid "solid framework," one does not quite see how the osmotic pressure is necessary to keep it extended. It appears, however, that this precipitation theory can be extended to drying, the solid framework growing by accretion as the concentration changes in the liquid phase, and building up the skin extension to which we have referred.

<sup>9</sup> H. R. Procter, Ref. 3. Also Procter and J. A. Wilson, *J. Chem. Soc.*, 109, 307 (1916). J. A. Wilson and W. Wilson, *THIS JOURNAL*, 40, 886 (1918). J. Loeb, *J. Gen. Physiol.*, 1918-1921; *Science*, 52, 449 (1920).

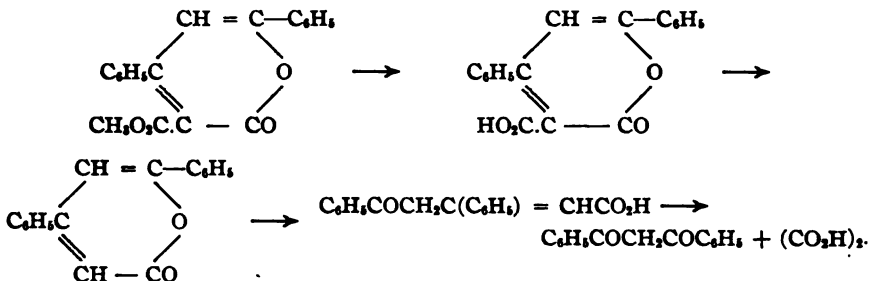


a means of detecting acetylenic ketones in alkaline media in which they are rapidly transformed into other substances.

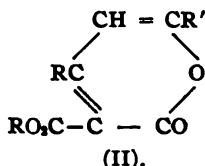
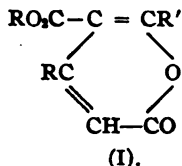
The addition of metallic derivatives to acetylenic ketones does not seem to have been tried heretofore; but Michael<sup>1</sup> found that sodium malonic ester combines with esters of acetylenic acids, and the extensive researches of Moureu<sup>2</sup> have shown that acetylenic ketones combine with other substances even more readily than do the corresponding ethylenic compounds. It was to be expected, therefore, that in the presence of sodium alcoholate, malonic ester would combine with benzoyl-phenylacetylene in accordance with the equation,



The experiment showed that addition takes place rapidly in the direction expected, but that the product immediately loses alcohol and passes into a pyrone derivative. The structure of the resulting product was established by the following series of transformations:



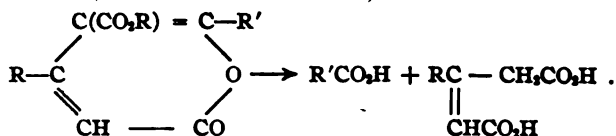
These transformations show that the product is an  $\alpha$ -pyrone derivative and that the course of the reaction is similar to that observed by Ruhemann when he added ketonic esters or diketones to esters of phenylpropionic acid. The products of the two reactions, however, never have the same structure. Thus the addition of a ketonic ester to an acetylenic ester gives a pyrone derivative which has the ester group in the 5 position (Type I) while the same group occupies the 3 position in the products obtained by adding an ester to an acetylenic ketone (Type II).



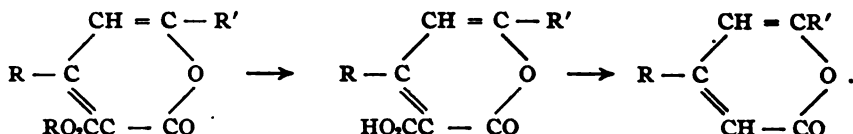
<sup>1</sup> Michael, *J. prakt. Chem.*, [2] 49, 22 (1894).

<sup>2</sup> Moureu, *Bull. soc. chim.*, [3] 33, 131 (1905).

Pyrone derivatives of the first type have long been known. It is impossible to hydrolyze them without opening the ring. On treatment with alkalis they lose a molecule of acid and give substituted glutaric acids.



Derivatives of the second type have not been described heretofore. They can be hydrolyzed without breaking the pyrone ring. On treatment with alkalis they give either the pyrone acid or the corresponding pyrone.



This characteristic behavior towards alkalis, which is analogous to that of the corresponding open-chained compounds, serves as an easy means of identifying substances belonging to either of these types of pyrone derivatives.

The  $\alpha$ -pyrone esters are moderately soluble in organic solvents, crystallize extremely well, and separate readily even from solutions that hold large quantities of oily products. As their structure is easily determined, they are admirably adapted for detecting and identifying acetylenic ketones.

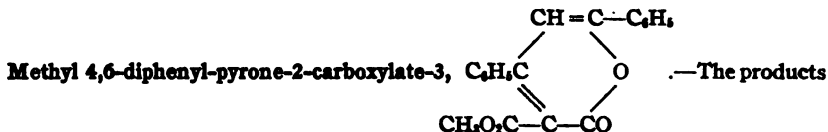
### Experimental Part.

**Condensation.**—The simplest way to carry out the condensation is to add a small quantity of sodium alcoholate to a warm, concentrated, alcoholic solution containing equivalent quantities of ester and unsaturated ketone. The liquid immediately becomes blood-red in color, the temperature rises to the boiling point of the liquid, and the reaction is complete by the time the liquid has cooled to the ordinary temperature. Most of the pyrone separates in an almost pure state when the solution is acidified with acetic acid. The balance is obtained by pouring the filtrate into water, extracting with ether, removing a small quantity of acid by shaking with sodium carbonate, and allowing the ether to evaporate.

The procedure was varied in a number of ways in an effort to prevent the pyrone formation and thus get the unsaturated dibasic ester which is, doubtless, the primary product of the reaction. Thus, ether and benzene were substituted for the alcohols as solvents, suspensions of sodium malonate were used in place of malonic ester and sodium alcoholate, and the temperature was reduced to the lowest point at which the reaction would proceed; but the results were essentially the same in all cases: 70 to 95%

of the product was pyrone ester, the balance consisting of variable quantities of pyrone acid due to hydrolysis, and of dibenzoyl-methane formed by the action of alkali on benzoyl-phenylacetylene.

When the sodium derivative of malonic ester was used in ether or in benzene, a brilliant red sodium compound separated as the reaction proceeded. Since the same compound was obtained by adding conc. sodium alcoholate to solutions of the pyrone ester in the same solvents, it is evident that the pyrone is formed under the influence of the alkali and not during acidification. It is not necessary to use pure benzoyl-phenylacetylene for the preparation of the pyrone ester. The crude washed and dried product of the reaction between sodium phenylacetylene and benzoyl bromide, which usually contains less than 60% of unsaturated ketone, serves equally well, and it is thus possible to avoid the serious losses involved in the vacuum distillations of this product.



obtained by condensing dimethyl malonate with benzoyl-phenylacetylene crystallize in long, pale yellow, fluorescent needles which melt at 129°.

*Analysis.* Calc. for  $\text{C}_{18}\text{H}_{14}\text{O}_4$ : C, 74.5; H, 4.6. Found: C, 74.6; H, 4.7.

The ester is readily soluble in acetone and in chloroform, moderately in ether and in methyl alcohol, sparingly in ligroin. Under diminished pressure it distils without decomposition. The pyrone ring is not opened by acids; a suspension of 2 g. of the ester in methyl alcohol was saturated with hydrogen chloride, sealed in a tube, and kept for over a year; but the only change was a small amount of hydrolysis to the corresponding acid. The ester dissolves readily in conc. sulfuric acid, and is precipitated unchanged when the orange colored solution is diluted with water or alcohol.

The ~~ETHYL ESTER~~ was obtained in the same way as the methyl compound which it closely resembles in color, in crystal form, and in solubility. It melts at 119°. Neither this nor the methyl ester reduces a solution of permanganate in acetone, or combines with bromine.

*Analysis.* Calc. for  $\text{C}_{20}\text{H}_{16}\text{O}_4$ : C, 75.0; H, 5.0. Found: C, 74.8; H, 5.1.

The ACID. The pyrone esters are exceedingly sensitive to alkalis. They dissolve in cold aqueous and alcoholic potash forming blood-red solutions which rapidly turn yellow. These yellow solutions contain small quantities of the corresponding acid, with relatively much malonic acid, dibenzoyl-methane, benzaldehyde and other decomposition products. Under these conditions, evidently, the addition reaction is reversed and the products noted result from the action of alkalis on malonic ester and benzoyl-phenylacetylene. Cold alcoholic sodium alcoholate causes less extensive decomposition, but gives only a minimal quantity of acid products. A fairly satisfactory hydrolysis to the pyrone acid was finally accomplished as follows. A solution of either ester in excess of cold conc. sodium methylate was diluted with 8 to 10 times its volume of benzene and the mixture boiled on a steam-bath. It rapidly lost its red color and deposited an impure yellow sodium salt. This was recrystallized from a strong solution of sodium carbonate in which it is sparingly soluble and from which it separates in

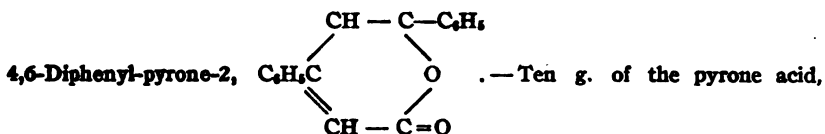
colorless plates. The yield of pure salt was 70%. The corresponding acid was purified by crystallization from benzene which deposits it in stout needles that contain benzene of crystallization.

*Analysis.* Calc. for  $C_{18}H_{15}O_4 \cdot C_6H_6$ : C, 77.7; H, 4.8. Found: C, 76.8; H, 4.7.

In the air these crystals lose benzene and crumble to a yellow powder which melts at  $168^\circ$ .

*Analysis.* Calc. for  $C_{18}H_{15}O_4$ : C, 74.0; H, 4.1. Found: C, 73.6; H, 4.1.

The yield of pure acid was about 70%. Neither the pyrone acid nor its salts reduce permanganate at the ordinary temperature. The acid begins to decompose at about  $200^\circ$ ; it gives off carbon dioxide freely above  $210^\circ$ .



when heated for 2 hours at  $210$ – $212^\circ$  gave 8.39 g. of a pale yellow melt which crystallized when rubbed with a little methyl alcohol, and 7.69 g. of pure pyrone melting at  $142^\circ$ .

*Analysis.* Calc. for  $C_{17}H_{14}O_2$ : C, 82.3; H, 4.8. Found: C, 82.0; H, 5.1.

The same substance can be obtained more easily directly from the pyrone esters. Thus 5 g. of the methyl ester was suspended in a solution of 1.2 g. of sodium in 20 cc. of dry methyl alcohol and the mixture set aside until the red color had completely disappeared. Meanwhile, the liquid had deposited 1.5 g. of pure pyrone and, when the filtrate from this was diluted with water, it yielded 1.6 g. more of slightly less pure material. The pyrone crystallizes in pale yellow plates which are moderately soluble in alcohol, sparingly in ether. Its solution in acetone does not reduce permanganate.

$\gamma$ -Benzoyl- $\beta$ -phenyl crotonic acid,  $C_6H_5COCH_2C(C_6H_5):CHCO_2H$ .—The pyrone is not attacked by conc. aqueous potassium hydroxide. It dissolves readily, however, both in alcoholic potash and in a solution of sodium methyrate. From the resulting yellow solutions, acids precipitate a mixture of 2 colorless acids extremely difficult to separate. By repeated recrystallization from ether-ligroin mixtures, one of these was obtained in a pure condition. It crystallized in slender needles which melted, with effervescence, at about  $130^\circ$ .

*Analysis.* Calc. for  $C_{17}H_{14}O_2$ : C, 76.7; H, 5.2. Found: C, 76.4; H, 5.2.

**THE METHYL ESTER.** The purity of the acid was established by esterification through the silver salt. With methyl iodide this gave, in calculated amount, a solid methyl ester which crystallized in needles and melted at  $36^\circ$ .

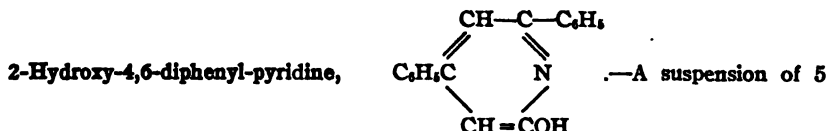
*Analysis.* Calc. for  $C_{18}H_{16}O_2$ : C, 77.1; H, 5.7. Found: C, 76.7; H, 5.8.

**Oxidation.**—Both the acid and its methyl ester are readily oxidized by permanganate. When the oxidation is carried out in acetone, the entire carbon chain is destroyed and the only products are benzoic and oxalic acids. By cautious oxidation of the sodium salt in aqueous solution, however, it is possible to confine the action of the oxidizer largely to the double linkage. Thus 2.5 g. of the acid was dissolved in excess of sodium hydrogen carbonate, the solution saturated with carbon dioxide at  $0^\circ$ , and treated, gradually, with a solution of 3 g. of permanganate, a current of carbon dioxide being maintained throughout the operation. The oxides of manganese were then dissolved with sulfur dioxide and the organic products extracted from the water solution with ether. The ethereal solution was shaken, first with sodium carbonate to remove acids, and then with a solution of copper acetate. This precipitated a green copper compound which melted, with decomposition, at about  $300^\circ$ .

The copper compound was suspended in ether and decomposed with dil. hydrochloric acid. The ethereal layer, on evaporation, deposited 0.9 g. of colorless needles that melted at 81°. A mixture of the substance with dibenzoyl-methane likewise melted at 81°.

The second acid that is formed when the pyrone ring is opened with alkalis was not obtained in a perfectly pure condition. An analysis of the mixture of the two acids gave: C, 76.8%, and H, 5.9%. The 2 acids are, therefore, certainly isomeric, and there are some indications that one readily passes into the other; but whether the isomerism is spatial or structural remains in doubt. These acids are still under investigation. They are the only known unsaturated  $\delta$ -ketonic acids—a type that is of especial interest in connection with the peculiar isomerism of the glutaconic acids.

**Action of Ammonia on the Pyrone Esters.**—It is well known that ammonia transforms many pyrones into the corresponding hydroxy pyridines; but Ruhemann found that when  $\alpha$ -pyrones which have hydrocarbon residues in the  $\alpha'$  position are heated with conc. aqueous ammonia they generally give ammonium salts of amino compounds. The structure of these salts is uncertain, and they can be turned into pyridine derivatives only by roundabout methods. The  $\alpha$ -pyrone esters described in this paper give a similar result when they are heated with aqueous ammonia, but when they are shaken at the ordinary temperature with conc. alcoholic ammonia they pass slowly but completely into a mixture of hydroxy-pyridine esters and the corresponding hydroxy-pyridine. At the ordinary temperature, conc. aqueous ammonia acts very slowly, but in the course of several months it transforms these  $\alpha$ -pyrone esters quantitatively into the hydroxy-pyridine derivative.

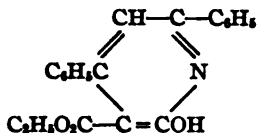


g. of the ethyl ester in 20 cc. of saturated alcoholic ammonia was shaken for 48 hours. By this time the dark yellow color which developed on the addition of the alcoholic ammonia had largely disappeared and the liquid had deposited a fine white powder. This was filtered off and the filtrate evaporated in a draught. The solid consisted mainly of the hydroxy-pyridine. It was purified by recrystallization from alcohol from which it separated in colorless or very pale yellow plates that melted at 210°.

**Analysis.** Calc. for  $C_{17}H_{15}ON$ : C, 82.6; H, 5.3. Found: C, 82.2; H, 5.5.

The substance is soluble in acids and in alkalis. It is doubtless identical with a substance previously obtained by Von Meyer.

**Ethyl-2-hydroxy-4,6-diphenyl-pyridine carboxylate-3,**



The residue left after evaporating the filtrate from the hydroxy-pyridine consists largely of this ester, which is more sparingly soluble in alcohol but much more readily soluble in alcoholic ammonia than the corresponding hydroxy-pyridine. The ester crystallizes from alcohol in colorless pyramids or prisms which show a faint blue fluorescence and melt at 197°. It dissolves in strong alkalis, but not in acids. Its solutions in conc. aqueous sodium hydroxide and in alcoholic ammonia are pale yellow in color.

*Analysis.* Calc. for  $C_{20}H_{17}O_2N$ : C, 75.1; H, 5.3. Found: C, 74.9; H, 5.6.

When the ester is heated with conc. aqueous potassium hydroxide it is converted into a mixture of the corresponding acid and the hydroxy-pyridine. The acid readily loses carbon dioxide at  $250^\circ$  and passes quantitatively into the same hydroxy-pyridine.

### Summary.

1. Under the influence of sodium alcoholate, benzoyl-phenylacetylene rapidly condenses with malonic esters to form pyrone esters that have an ester group in the 3 position.

2. Pyrone esters which have the ester group in the 3 position are readily distinguished from those which have this group in the 5 position by their behavior towards alkalis.

3. By opening the ring of an  $\alpha$ -pyrone which has phenyl groups in the 3 and 6 positions it is possible to get unsaturated  $\delta$ -ketonic acids which have the carbon chain that is responsible for the peculiar isomerism of the glutaconic acids.

CAMBRIDGE 38, MASSACHUSETTS.

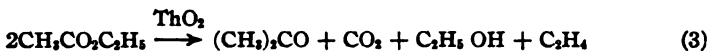
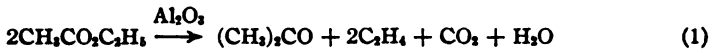
[CONTRIBUTION FROM THE LABORATORY OF ORGANIC CHEMISTRY OF THE UNIVERSITY OF WISCONSIN.]

## THE ACTION OF ALUMINA, TITANIA AND THORIA UPON ETHYL AND ISOPROPYL ACETATES.

BY HOMER ADKINS AND A. C. KRAUSE.

Received November 16, 1921.

It has seemed that a more intensive, quantitative study of some of the gas-phase reactions of organic compounds induced by catalysts might shed some light upon the mechanism of catalysis. In view of the widely different decompositions which, according to Sabatier, are induced in esters by alumina, titania and thoria, it was suggested by Dr. Wilder D. Bancroft that these reactions offered a fruitful field for study. Sabatier<sup>1</sup> reports that alumina induces Reaction 1; titania, 2; and thoria, 3.



If these equations accurately represent the decompositions, we have a very specific reaction for each catalyst, and it was hoped that it would be possible to find some connection between the properties of the catalyst and the reaction induced. Our results do not indicate that the catalysts are highly specific, but we have found that the decomposition of the esters offers the possibility of a comparative study of the same catalyst upon

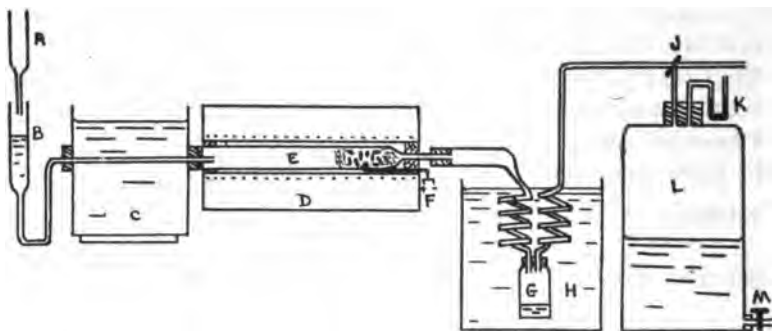
<sup>1</sup> Sabatier "La Catalyse en Chemie Organique," Van Nostrand Co., 1920, p. 341.

two distinct reactions; that of decarboxylation and of dehydration, under conditions which are automatically identical for such variables as "space-time-velocity" and concentration.

### Experimental Part.

The apparatus and method of procedure were similar to those used by Engelder.<sup>2</sup> A sketch of the apparatus is shown in Fig. 1.

The ester was introduced from the buret A into the reservoir B, the outlet from which led through a boiling water-bath into the catalyst tube E. This latter consisted of a Pyrex glass tube 2×42 cm. constricted to a diameter of 5 mm. at its outlet end.



The tube contained an indentation for the head of the thermocouple F at a point 2 cm. from the constriction and 4 cm. from the outlet end of the electrically-heated furnace D. The catalyst in the form of pills was placed around the indentation and held in place by glass beads and glass wool. Asbestos paper was wrapped around the tube and thermocouple. The products of the reaction passed through the spiral condenser into the receiver G in which the liquid products were collected. The receiver G and the condensers were immersed in an ice-bath. The gaseous products passed out through the second condenser and were collected over a saturated salt solution in the 7.5-liter bottle L, which was provided with a manometer K.

The thermocouple was connected to a Leeds and Northrup potentiometer, recorder and controller<sup>3</sup> which automatically regulated the temperature of the furnace to  $\pm 2^\circ$ .

The gas formed by the decomposition of ethyl acetate was analyzed according to the usual methods. (1) The *carbon dioxide* was absorbed in (1:1) potassium hydroxide contained in a Hempel single pipet. (2) *Ethylene* was absorbed in a water solution of bromine contained in a Hempel double pipet. The bromine fumes were removed with potassium hydroxide. (3) *Carbon monoxide* was absorbed in an acid solution of cuprous chloride.<sup>4</sup>

The distillate was analyzed by the standard methods. (1) *Acetic acid*: about 2 g. of weighed distillate was mixed with about 100 cc. of water and titrated at once with a standard 0.5 N solution of sodium hydroxide. (2) *Ethyl acetate*: a weighed sample was saponified in a standard (0.5 N) alcoholic solution of potassium hydroxide, contained in a pressure bottle, held in a boiling water-bath for 45 minutes. The excess of alkali was

<sup>2</sup> Engelder, *J. Phys. Chem.*, **21**, 679 (1917).

<sup>3</sup> Funds for the purchase of this apparatus were allotted by the Research Committee of the University of Wisconsin upon the recommendation of Dean C. S. Slichter and Dr. J. H. Mathews.

<sup>4</sup> Krauskopf and Purdy, *J. Ind. Eng. Chem.*, **12**, 158 (1920).

titrated with a 0.5 *N* sodium hydroxide solution using phenolphthalein as indicator. (3) *Acetone*: about 0.4 g. of weighed distillate was dissolved in 100 cc. of water to which had been added 50 cc. of a 0.5 *N* solution of sodium hydroxide. After standing for 10 minutes, a 0.4 *N* solution of iodine in potassium iodide solution was added drop by drop until at least a 25% excess had been added. After standing for 10 minutes, the acid equivalent of the alkali solution was added and the excess iodine titrated with a 0.5 *N* solution of sodium thiosulfate using starch as an indicator.

### The Preparation of the Catalysts.

Three hundred g. of hydrated aluminum nitrate,  $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ , was dissolved in 2 liters of distilled water. The solution was heated to boiling and conc. ammonium hydroxide added until precipitation was complete. The solution was diluted to 8 times its original volume, heated to boiling for 15 minutes and allowed to cool. The precipitate was then washed with distilled water by decantation until free from ammonium nitrate. It was filtered off and dried in a hot-air oven at 165°. Catalysts were also prepared from the sulfate in the same general way.

*Thoria* was prepared by ignition of the nitrate and also by the precipitation of thorium hydroxide as indicated for alumina.

*Titania* was prepared by dissolving the oxide in hot conc. sulfuric acid, diluting with 10 volumes of water and precipitating as with alumina. This catalyst was also made by precipitating blue titanous hydroxide from a solution of titanic chloride and allowing it to oxidize, in the solution, to the white hydroxide.

The catalysts were made into pellets with a pill machine. These were of such a size that 20 of them (the unit charge) weighed about 2.5 g. We believe that by the use of the catalyst in this form it may be placed in the tube to better advantage than when used as a powder. Its catalytic activity is not impaired by this treatment. It was interesting to note that apparently as much reaction took place in the center of the pellets as at the surface. This was evidenced by the equal deposition of carbon throughout the pellet.

### Notes on Catalysts Used.

Runs 1-5. An alumina catalyst prepared from the sulfate. The sulfur compounds had been removed by passage of a few cubic centimeters of ester over the heated catalyst. The catalyst had been dried for 24 hours at the temperature of the reaction. In all the runs in which alumina (or ignited titania) was used there was 3-4% of hydrogen and saturated hydrocarbons in the gaseous products.

Runs 6-10. An alumina catalyst prepared as for Runs 1-5. 45 cc. of ethyl acetate was passed over the catalyst between Runs 8 and 9.

Runs 11-12. The catalyst was a sample of titania obtained from the Will Corporation.

Runs 13-14. An alumina catalyst prepared from the nitrate. It was dried at the temperature of the reaction for 12 hours.

Run 15. Same as for Runs 13-14.

Runs 16-17. Same as Runs 1-5, 6-10. *Isopropyl* acetate used instead of ethyl acetate.

Runs 18-19. An ignited thoria catalyst. It was dried overnight at the temperature of reaction. The catalyst was heated at 455° for 6 hours between Runs 18 and 19. There was 9-12% hydrogen and saturated hydrocarbons in the gaseous products.

Run 20. Catalyst prepared as for Runs 18-19. *Isopropyl* acetate was used. There was no hydrogen in the gaseous products.

Runs 21-22. Titania prepared from sulfate. Ethyl acetate used in 21 and *isopropyl* acetate in 22. Gas showed 17% ethane and 6% hydrogen in 21.



Run 23. Titania from the same sample as that used for Runs 21-22 but which had been ignited for an hour at red heat. There was 14% ethane in the gas.

Runs 24-25. The catalyst was that used in Runs 1-5 and later ignited at red heat for 2 hours.

Runs 26-27. Titania prepared from titanium trichloride. Gas contained 13% hydrocarbons in Run 26 when ethyl acetate was used. Isopropyl acetate was used in Run 27.

Run 28. Thoria prepared from nitrate by solution and precipitation as hydroxide with subsequent drying at the temperature of reaction. There was 5-6% of hydrogen and hydrocarbons in the gaseous products. After ignition of this catalyst its ethylene efficiency had been reduced with a consequent rise in the amounts of saturated hydrocarbons formed.

Run 29. An alumina catalyst dried overnight at the temperature of reaction. A molecular mixture of 45 g. of alcohol and acetic acid was substituted for the ethyl acetate.

Run 30. An alumina catalyst dried for 24 hours at the temperature of reaction.

Run 31. An alumina catalyst, not previously dried at the temperature of reaction.

### Explanation of Table.

In calculating the equivalents of the products of the reaction, it is assumed that 2 molecules of ethyl acetate are equivalent to 2 molecules of ethylene, 1 of acetone, 2 of acetic acid, and 1 of carbon dioxide. (See Equations 1 and 2). Col. 15 of the table gives in percentages the amounts of acetone found in the distillate as compared with the amount that should have been there if one molecule of carbon dioxide is formed for each molecule of acetone.

Col. 17 gives in percentages the degrees to which the relative production of carbon dioxide and ethylene satisfy the requirements of Equation 1. The percentage of the total number of molecules decomposed that produce carbon dioxide (and acetone) is given in Col. 20 of the table. The same information in regard to ethylene is given in Col. 21. These figures may be taken as representing the efficiency of the catalyst in these two phases of the reaction.

### Discussion.

The question arises as to the extent to which the results here recorded agree with the general statements of Sabatier<sup>1</sup> as to the specificity of the catalysts for inducing decompositions. If the alumina induces Reaction 1, then the volume of ethylene should be twice that of the carbon dioxide. Analyses of the effluent gas made within a few minutes of the beginning of a run indicated that such a ratio was approximated. However, the percentage of carbon dioxide in the gas rapidly decreased to an amount which was rather characteristic of the method of preparation of the catalyst and its subsequent treatment. The figures in Col. 20 of the table indicate that upon use the efficiency of an alumina catalyst for the production of carbon dioxide (and of acetone) decreases while the efficiency of the catalyst for the production of ethylene is not much changed (Col. 21). A fresh

TABLE I.—ANALYTICAL DATA

Run	Ester intro-duced	Ester recov-ered	Ester decomposed	Distillate	AcOH	MeCO	CO <sub>2</sub>	CH <sub>4</sub>	CO	Ester = CO <sub>2</sub>	Ester = AcOH	Ester = CO <sub>2</sub> + AcOH	MeCO recovered	Ester = H <sub>2</sub>	Reaction A	Duration of run	Temp.	CO <sub>2</sub> ciency	C <sub>2</sub> H <sub>4</sub> eff-iciency
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20
1	38.7	3.0	35.7	18	3.8	5.2	7.6	11.4	0.10	30.4	5.5	35.9	15.8	52	35.8	80	141	455	100
2	42.7	4.9	37.7	21	5.56	5.7	7.3	11.7	0.20	29.2	8.1	37.3	59	36.7	80	123	457	78	97
3	42.3	7.2	35.1	24	6.25	5.3	6.6	11.0	0.22	26.4	9.1	35.5	16.1	61	34.5	77	135	454	75
4	42.3	6.6	35.7	24	8.40	5.3	6.1	11.1	0.20	24.4	12.9	37.3	16.1	66	34.9	72	138	454	69
5	45.0	6.9	38.1	25.5	7.65	5.0	6.4	11.7	0.20	25.6	11.2	36.8	15.2	60	36.7	71	130	455	67
6	33.3	5.6	27.7	18.5	5.10	3.8	5.35	8.40	0.10	21.6	7.5	29.1	11.5	53	26.4	82	130	417	95
7	42.3	15.7	26.6	31	7.60	3.7	4.6	7.9	0.15	18.4	11.1	29.5	11.2	67	24.8	74	100	417	69
8	40.0	9.6	30.4	25.5	8.30	3.7	4.6	9.7	0.15	18.4	12.1	30.5	11.2	75	30.4	60	128	417	100
9	42.3	8.2	34.1	28	14.10	3.7	3.5	10.5	0.25	15.0	20.6	35.6	11.2	67	33.0	45	120	455	44
10	44.5	8.7	35.8	29	15.8	2.4	2.7	11.4	0.25	10.8	23.1	33.9	7.3	68	35.8	30	113	455	30
11	41.4	10.7	30.7	29	13.3	1.9	2.4	9.5	0.25	9.6	19.4	29.0	5.8	60	29.8	32	105	455	31
12	39.6	...	...	...	16.9	0.3	6.9	11.1	...	27.6	24.7	...	0.9	...	...	...	120	455	...
13	36.5	2.5	34.0	17	5.0	4.1	6.9	11.1	0.10	27.6	7.4	35.0	12.3	45	34.9	81	120	455	...
14	42.0	5.5	36.5	25	12.9	3.9	3.7	10.9	0.35	14.8	19.0	33.8	11.7	80	34.2	45	139	455	41
15	44.0	11.1	32.9	27	6.9	4.5	6.0	10.1	0.10	24.0	10.1	34.1	13.5	56	31.7	76	120	455	73
16	43.0	1.5	41.5	19	8.7	4.6	6.4	16.1	...	29.6	14.8	44.4	16.2	55	39.1	75	120	455	71
17	45.0	2.0	43.0	20	9.7	4.6	5.6	16.8	...	25.9	16.5	42.4	16.2	63	40.8	63	102	455	60
18	41.0	9.0	32.0	30	0.3	6.0	7.8	2.4	0.55	31.2	0.45	31.7	18.2	58	7.5	...	105	455	97
19	42.0	7.9	34.1	31	0.2	7.9	8.0	2.6	0.40	32.0	0.3	32.3	24.0	75	8.2	...	103	455	92
20	40.0	3.1	36.9	20.0	0.35	7.8	7.4	11.6	0.20	34.3	0.6	34.9	27.4	76	28.2	...	105	455	93
21	46.0	30.0	16.0	39.0	2.6	1.6	2.4	2.3	0.20	9.6	3.8	13.4	4.8	50	7.2	...	95	455	60
22	44.0	20.0	24.0	35.0	11.7	0.7	1.2	8.4	...	5.5	19.9	24.4	2.5	45	20.5	...	90	455	23
23	43.0	38.0	5.0	41.0	1.6	0.2	0.5	1.0	0.04	2.0	2.3	4.3	0.7	35	3.1	...	80	455	40
24	38.5	17.4	21.1	29.0	4.6	3.5	3.4	5.7	...	13.6	6.8	20.4	10.5	80	17.9	67	140	455	64
25	35.5	14.7	20.8	26.0	5.2	3.7	3.4	5.8	...	17.6	7.6	21.2	9.9	73	18.2	63	129	455	65
26	43.0	16.8	26.2	93.0	5.0	3.3	4.4	7.1	0.10	17.6	7.4	25.0	11.3	60	40.6	79	100	455	75
27	44.0	1.4	42.6	18.5	5.4	5.2	6.9	17.1	...	31.9	9.2	41.1	19.3	65	51	...	340	455	94
28	87.0	14.6	72.4	49.0	5.3	12.0	17.0	18.0	0.50	68.0	7.8	75.8	36.5	51	56.5	...	105	455	...
29	37.3	9.4	27.9	40.0	14.7	2.0	2.8	5.5	...	11.3	21.5	32.8	6.1	53	17.3	...	105	455	...
30	270.0	106.4	163.6	190.0	46.4	12.9	23.7	50.4	...	94.8	68.2	163.0	39.0	41	158.3	59	991	455	58
31	127.0	32.3	94.7	81.2	21.3	6.5	13.2	25.4	...	52.8	30.7	83.5	19.8	37	79.8	70	434	455	65
32	29 g. of acetone over alumina at 455° in 1 hour. 65% of the acetone was recovered in the distillate. Negligible amount of gas.																		
33	40.0 of "commercial acetone" containing 24 g. of (CH <sub>3</sub> ) <sub>2</sub> CO passed over alumina at 455° during 3 hours.																		

alumina catalyst in a 2-hour run split carbon dioxide out of 80% (Run 1) or 78% (Run 6) of the molecules decomposed. In the case of a catalyst (Run 10) which had previously been used 6 times, the efficiency for the production of carbon dioxide had fallen to 30% while the efficiency as an ethylene producer was still in the vicinity of 100%. The degree to which Reaction 1 was induced (Col. 17 of the table) was 80% to 82% (Runs 1 and 6) in the first run and then fell off until in Run 10 only 30% of the activity of the catalyst was manifested in the production of this reaction. Ignition of such a catalyst restored to it the property of producing carbon dioxide and ethylene in the former ratio, but the catalyst decomposed only  $\frac{1}{2}$  to  $\frac{2}{3}$  as much ester in a given length of time as did a fresh catalyst (Runs 24 and 25).

A titania catalyst (Run 11) showed itself to be 31% efficient in the production of carbon dioxide and 97% efficient in producing ethylene. This result is almost identical with that obtained by the use of a used alumina catalyst in Run 10. On the other hand, a titania catalyst (Run 26) prepared from titanous chloride ( $\text{TiCl}_3$ ) by precipitation of the blue titanous hydroxide, and then oxidizing this to the titanic hydroxide gave a result which is very similar to that obtained with a fresh alumina catalyst; that is, the catalyst was 67% efficient in producing carbon dioxide and 90% efficient in producing ethylene. In Run 27, in which *isopropyl* acetate was the ester used, the efficiency was 75% for carbon dioxide and 95% for propylene, the reaction going according to Equation 1 to the extent of 79%, a value which is very nearly the same as that obtained with a fresh alumina catalyst.

A thoria catalyst (Run 18) prepared by the ignition of the nitrate gave a result similar to the one obtained by Sabatier. It showed a 97% efficiency in the production of carbon dioxide and 23% for ethylene.

A thoria catalyst (Run 28) which had been prepared by precipitation of the hydroxide was approximately as efficient as a carbon dioxide-acetone producer as was the ignited thoria (Run 18) catalyst, but it was much more effective in the production of ethylene. It showed an efficiency of 94% as a carbon dioxide producer and 78% for ethylene, the latter figure being more than three times as large as that for the ignited catalyst and approaching in magnitude that obtained for alumina.

The comparisons just made of the various catalysts have not involved any consideration of the amounts of acetic acid and acetone produced. In Col. 13 of the table is given the sum of the amounts of the ester equivalent to the carbon dioxide and acetic acid found. This amount is in most runs approximately equal to the amounts of ethyl acetate decomposed (Col. 4). This indicates that a decrease in carbon dioxide production is accompanied by an equivalent increase in the amount of acetic acid. Col. 15 of the table gives in percentages the amount of acetone found in the

distillate as compared to the amount that should have been there if the weight of carbon dioxide obtained had been taken as the basis of the calculation. It may be seen that the recovery in the case of a fresh alumina catalyst prepared from the sulfate is 52% or 53% (Runs 1 and 6) and 45% in the catalyst prepared from the nitrate (Run 13). Upon continued use of the catalyst, the acetone recovery increases in several cases to over 70%. The distillate becomes lighter in color and supposedly the condensing power of the alumina for the acetone becomes less. That alumina does have a condensing action upon acetone is shown by Runs 32 and 33. Only 62 to 65% of the acetone passed over the catalyst was recovered unchanged. That the action was a condensing one is indicated by the facts that with the pure acetone (Run 32), (1) only a small amount of gas was formed, (2) the weight of the distillate was only one gram less than the weight of the acetone introduced, and (3) the distillate showed no acidity and contained products boiling from 150° to 275°.

Runs 30 and 31 were made with the object of determining the effect on the efficiency of the catalyst of long continued runs and of previous drying of the catalyst at the temperature at which it was later to be used as a catalyst. During the period of the runs there was no marked change in the ratio of the gases produced by the decomposition. The results given below are the averages of the observations made during 7-hour periods.

Run 30 (dried catalyst): gas per cc. AcOEt, 199 cc. (42 cc. of CO<sub>2</sub>, 148 cc. of C<sub>2</sub>H<sub>4</sub>); ratio 1:3.5.

Run 31 (undried catalyst): gas per cc. AcOEt, 245 cc. (58 cc. of CO<sub>2</sub>, 175 cc. of C<sub>2</sub>H<sub>4</sub>); 1:3.0.

These results show that the undried catalyst is more active in the production of both gases but much more so with respect to carbon dioxide (26%) than with respect to ethylene (11%).

In all of the work discussed the production of the unsaturated hydrocarbon seems to vary independently of the production of acetone, acetic acid, or carbon dioxide. This indicates that the decomposition studied is that of the acid (or acid residue) and of the alcohol (or alcohol residue) rather than that of the ester. It seems that saponification of the ester precedes decomposition. A further study of the saponification of esters in the gas phase is anticipated.

Sabatier<sup>6</sup> explains that the difference in the decomposition of esters by various catalysts is due to the relative stabilities of the intermediate compounds formed between the catalyst and the acid and the catalyst and the alcohol. For example, if the instability of the two temporary compounds is of the same order, then the reaction goes according to Equation 1. If the salt of the alcohol is more rapidly decomposed than that of the acid,

<sup>6</sup> Ref. 1, *Compt. rend.*, 152, 669 (1911).

the water so formed reacts with the salt of the acid, liberating the acid, and the reaction goes according to Equation 2. It is difficult for us to believe that thorium ethoxide is more unstable when the catalyst is prepared from the nitrate by precipitation than it is when the catalyst is prepared from the nitrate by ignition, or that titanium acetate is more unstable when the catalyst is prepared in solution than when it is prepared in some other way. Yet it would seem necessary to make this assumption in order to explain our experimental results according to Sabatier's theory.

### Summary.

1. Experimental confirmation of the statement that alumina, titania and thoria catalyze specific decompositions of ethyl acetate, has not been obtained. The results obtained by us indicate that in determining the order of efficiency of these catalysts for these reactions, the method of preparation of the catalyst is of equal if not of greater importance than the particular metallic element present in the catalyst.
2. Evidence is presented indicating that the course of the decomposition is not determined by the relative instability of the salts of the acid and of the alcohol.
3. The probabilities are that saponification of the ester precedes decomposition.
4. An unignited alumina catalyst prepared from the hydroxide exerts a strong condensing action upon acetone at 455°.

MADISON, WISCONSIN.

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[CONTRIBUTION FROM THE LABORATORIES OF THE TEXAS COMPANY.]

## A SIMPLER METHOD OF DETERMINING ACETYL VALUES.

BY LEON W. COOK.

Received November 18, 1921.

Lewkowitsch<sup>1</sup> defines the acetyl value as "the number of milligrams of potassium hydrate required for the neutralization of the acetic acid obtained on saponifying one gram of an acetylated fat or wax." The method for determining the acetyl value as outlined by Lewkowitsch has been adopted as the standard method of analysis. This method of obtaining the acetyl value by actual titration of the acetic acid used in acetylation, involving as it does the separation of this acetic acid by somewhat laborious means can be considerably improved. This value may be obtained more quickly and with greater accuracy by a knowledge of the saponification values of the oil before and after acetylation. This involves only an operation that is being continually performed in an oil laboratory.

<sup>1</sup> Lewkowitsch: "Chemical Analysis of Oils, Fats, and Waxes," Macmillan and Co., 5th ed., vol. 1, p. 428.

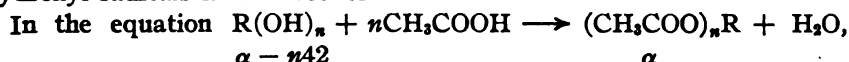
This method was first suggested by M. Émile André.<sup>2</sup> He gives the following formula,

$$A = S' - S \left( 1 + \frac{\lambda S}{1 - \lambda S} \right)$$

where  $A$  is the acetyl value;  $S$  the saponification value before acetylation;  $S'$  the value after acetylation, and  $\lambda$  is  $42/56 = 0.75$ .

To use this formula, we must define both acetyl and saponification values as g. instead of mg. of potassium hydroxide per g. of material. The latter (mg.) is the correct definition and the one given by André himself. It will be seen upon inspection that if  $S > 4/3$ , his acetyl value is negative. In order to use the values as correctly defined, we must give  $\lambda$  the value of  $0.042/56$  or  $0.00075$ . André's derivation of his formula is rather involved, employing the limit of a geometric series, and is confined to monohydric alcohols. Such a formula will be derived by simple algebra and the derivation will be extended to include polyhydric alcohols. By alcohol is meant any organic hydroxy compound which can be acetylated.

Let  $A$  be the acetyl value;  $S$ , the neutral saponification value before acetylation;  $S'$ , the value after acetylation;  $\alpha$ , the mol. wt. of acetate;  $x$ , the mg. of acetate in 1 gram of acetylated oil, and  $n$  the number of hydroxyl radicals in the alcohol.



the difference between the molecular weight of an alcohol and its corresponding acetate is  $n42$ . Every  $\alpha$  mg. of acetate corresponds to  $\alpha - n42$  mg. of alcohol in the oil, and every  $x$  mg. of acetate to  $x - \frac{n42x}{\alpha}$  mg. of alcohol; for  $\alpha : \alpha - n42 :: x : \text{mg. of alcohol}$ ; and therefore  $\text{mg. alcohol} = \frac{\alpha x - n42x}{\alpha} = x - \frac{n42x}{\alpha}$ .  $x$  Mg. of acetate represents a gain in weight in

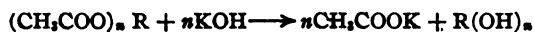
acetylation of  $\frac{n42x}{\alpha}$  mg. Thus 1000 mg. of acetylated material containing  $x$  mg. of acetate was obtained from  $1000 - \frac{n42x}{\alpha}$  mg. of original oil. So

if it takes  $S$  mg. of potassium hydroxide to saponify 1000 mg. of oil, it will take  $S \left( \frac{1000 - \frac{n42x}{\alpha}}{1000} \right)$  mg. to saponify  $1000 - \frac{n42x}{\alpha}$  mg. or the amount of original oil in 1000 mg. of acetylated material. The difference  $S' - S \left( 1 - \frac{n0.042x}{\alpha} \right)$  represents the difference between the alkali necessary

<sup>2</sup> André, *Compt. rend.*, 172, 984 (1921); *Bull. soc. chim.*, [4] 29, 745 (1921).

to saponify 1 g. of acetylated material and the alkali necessary to saponify the original oil contained in that amount. This difference is therefore the alkali necessary to neutralize the acetic acid obtained from 1 g. of acetylated oil or is the acetyl value.

$$A = S' - S \left( 1 - \frac{n0.042x}{\alpha} \right)$$



$$\begin{array}{ccc} \alpha & n56 & \\ x & A & \\ x:A = \alpha:n56 & \text{and } x = \frac{A\alpha}{n56} & \end{array}$$

Substituting

$$A = S' - S \left( 1 - \frac{n0.042 \frac{A\alpha}{n56}}{\alpha} \right) = S' - S \left( 1 - \frac{0.042}{56} A \right) = S' - S + \frac{0.042S}{56} A$$

$$A - \frac{0.042S}{56} A = S' - S, \quad A \left( 1 - \frac{0.042S}{56} \right) = S' - S$$

$$A = \frac{S' - S}{1 - 0.00075S}$$

By a similar derivation which I shall not give in detail the percentage of alcohol in the original sample may be found providing the molecular weight ( $M$ ) of the alcohol is known;

$$\% \text{ alcohol} = \frac{M(S' - S)}{560 - 0.42S'}$$

### Summary.

A formula has been derived by which the acetyl value of an oil may be calculated from the saponification value before and after acetylation. This method is quicker and more accurate than the one given in Lewkowitsch, commonly used. This formula has been used extensively in this laboratory with very satisfactory results.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE OHIO STATE UNIVERSITY.]

THE ACTION OF SELENIUM MONOCHLORIDE UPON PROPYLENE, BUTYLENE AND AMYLENE.<sup>1</sup>

BY C. E. BOORD AND F. F. COPE.

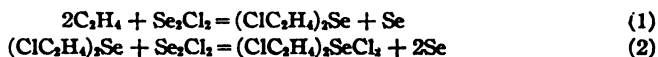
Received November 25, 1921.

Recent publications by Heath and Semon<sup>2</sup> and by Bauser, Gibson and Pope<sup>3</sup> make it desirable to publish an extension of work previously done in this laboratory.<sup>4</sup>

By passing ethylene into a solution of selenium monochloride, Heath and Semon obtained a white crystalline compound melting at 118°, which they have described as symmetrical tetrachloro-diethyl selenide. Bauser, Gibson and Pope by the same reaction obtained the crystalline compound melting at 122°, and have described it as  $\beta, \beta'$ -dichloro-diethyl selenide dichloride. Upon reducing this substance in water solution with sulfur dioxide they obtained  $\beta, \beta'$ -dichloro-diethyl selenide as a colorless oil which solidified when cooled. Basing their conclusions upon the nature of the products formed and upon the amount of selenium recovered these authors have represented the absorption of ethylene as follows.



Upon extending this reaction to the higher olefins, we have been able to show that the equation given above is the summation of two perfectly definite but consecutive reactions.



By passing the olefin into the selenium monochloride as the workers mentioned above have done, the ideal conditions for completing both stages are obtained. The action may be stopped at the end of the first stage by the simple process of reversing the order of bringing together the reagents.

## Preparation of Materials.

**Selenium Monochloride.**—The method described by Divers and Shimose<sup>5</sup> and used in a modified form both by Heath and Semon<sup>2</sup> and by Bauser, Gibson and Pope<sup>3</sup> is suitable for obtaining pure selenium monochloride. In this work the monochloride was always used in solution, so a more direct method was employed. Evans and Ramsay<sup>6</sup> have pointed out that selenium rapidly absorbs chlorine. This suggests the preparation of the chlorides of selenium by a method quite analogous to that used for the preparation of the chlorides of sulfur.

<sup>1</sup> Read before the Organic Section of the American Chemical Society at New York City, September 8, 1921. See *Science*, **54**, 526 (1921).

<sup>2</sup> Heath and Semon, *J. Ind. Eng. Chem.*, **12**, 1101 (1920).

<sup>3</sup> Bauser, Gibson and Pope, *J. Chem. Soc.*, 117, 1453 (1920).

<sup>4</sup> Burrell, *J. Ind. Eng. Chem.*, **11**, 101 (1919).

<sup>5</sup> Divers and Shimose, *J. Chem. Soc.*, **45**, 198 (1884).

<sup>6</sup> Evans and Ramsay, *ibid.*, **45**, 62 (1884).



In our earlier work the procedure used was as follows. A weighed quantity of finely divided metallic selenium was placed in a large round-bottom flask which had been provided with inlet and outlet tubes. A rapid current of dry chlorine was led in, close to the surface of the selenium. The absorption of chlorine was very rapid even at room temperature. The reaction took place with much heat evolution and the mixture became first pasty, then fluid and finally quite mobile. The rate of chlorination and the stirring were so adjusted as to avoid the formation of the yellowish-white incrustation of selenium tetrachloride on the walls of the flask and surface of the reaction mixture in so far as possible. Chlorination was stopped somewhat short of the gain in weight required to convert the selenium completely into the monochloride. The reaction mixture was now diluted with an indifferent solvent such as chloroform, carbon tetrachloride or benzene, filtered from undissolved selenium, and the solution of selenium chlorides thus obtained used for the interaction with the olefin.

In our later experiments the metallic selenium was suspended in one of the solvents mentioned above (benzene being used only after it had been shown that no appreciable amount of the chlorination products of benzene were formed) and chlorine led in with rapid stirring. In a typical run 200 g. of selenium was placed in a 1-liter flask and covered with 800 cc. of benzene. Chlorine was passed in rapidly until 89.46 g. (1 atom equivalent) had been absorbed. The absorption took place with the evolution of heat and almost no chlorine escaped from the reaction chamber. Filtration left a little unchanged selenium.

By neglecting the small amount of selenium dissolved unchanged one may calculate, from the weights of selenium used and recovered and weight of chlorine absorbed, the approximate amounts of selenium mono- and tetra-chloride formed. That such an approximation is justified is shown by the results obtained in the condensations described below.

**Olefins.**—Propylene, butylene and amylene were prepared from the corresponding monohydric alcohols by the contact process. The alcohol was admitted dropwise into the vertical arm of an iron tube 38 mm. in diameter and 120 cm. long mounted on a 21-burner combustion furnace. Anhydrous aluminum sulfate was used as the catalyst. In the preparation of amylene, amyl alcohol was passed through the tube at a temperature of 335°. The amylene was condensed, separated from the water, dried, and fractionated. The major portion boiled at 40–41°. Butylene was prepared from *N*-butyl alcohol at a temperature of 340° and had a purity of 92–95% by the bromine method. Propylene was prepared from *isopropyl* alcohol at a temperature of 360° with a purity of 90 to 91%.

### Experimental Part.

The logical condition for the direct preparation of *bis*( $\beta$ -chloro-alkyl) selenide is to bring the selenium monochloride into reaction with the olefin in such a way that the latter will be always in excess. This was accomplished by spraying the monochloride solution into an atmosphere of the olefin. The following general procedure was used.

A 2-liter, 3-necked Pyrex flask served as the reaction chamber. The large middle neck was provided with a 2-hole stopper bearing a stirring paddle and a dropping funnel. The stirring paddle was provided with a mercury seal and 2 sets of vanes, one for agitating the reaction mixture and one passing just below the tip of the dropping funnel for spraying the monochloride solution. Through one side-neck passed an inlet for the olefin and on the second was mounted a reflux condenser

To start the reaction, 200 cc. of anhydrous benzene was placed in the reaction chamber and violently agitated by mechanical stirring. The olefin was led in until the air was displaced and the solvent saturated. Selenium monochloride solution in benzene was now permitted to flow drop-wise from the dropping funnel onto the rapidly moving spray paddles at such a rate that the olefin could always be maintained in excess. The reaction was instantaneous, the walls of the flask becoming coated with amorphous selenium. After the addition of a measured quantity of the monochloride solution, the agitation was continued for a few minutes in the presence of the olefin and the operation interrupted. The reaction mixture was filtered rapidly by suction and the deposited selenium washed with anhydrous benzene, collected, dried and weighed. The filtrate was evaporated and the oily crude product purified by distillation under diminished pressure.

The general procedure for the direct preparation of *bis*( $\beta$ -chloro-alkyl) selenide dichlorides was much simpler. Here, it was sufficient that the olefin be led into the selenium monochloride solution until one mol had been absorbed. The reaction proceeded with heat evolution and sometimes required cooling. When the reaction was completed, the mixture was filtered warm and the deposited selenium washed repeatedly with warm benzene, dried and weighed. The combined filtrate and washings were evaporated to crystallization or to constant weight as the nature of the product required.

With the simpler olefins the second step in the reaction goes quite rapidly but with butylene and amylene it goes more slowly so that a longer time is required for the reaction to be completed.

***Bis*( $\beta$ -chloropropyl) Selenide.**—Three hundred cc. of a solution of selenium monochloride in benzene, containing 93 g. of selenium monochloride (64.2 g. of selenium) was led drop-wise into an atmosphere of propylene. Thirty-two g. or  $\frac{1}{3}$  of the selenium was recovered as free selenium. The oily crude product obtained upon evaporation of the filtrate was purified by distillation under diminished pressure. *Bis*( $\beta$ -chloropropyl) selenide was obtained as a lemon-yellow oil boiling at  $134^{\circ}$  under 10 mm. pressure.

The product was analyzed by digesting the sample with 20 cc. of 10% sodium hydroxide solution for 30 minutes, acidifying with nitric acid and titrating by the Volhard method.

**Analyses.** Calc. for  $C_6H_{12}Cl_2Se$ : Cl, 30.26. Found: 30.33, 30.24.

***Bis*( $\beta$ -chloropropyl) Selenide Dichloride.**—Dry propylene gas was led into a solution of 93 g. of selenium monochloride (64.2 g. of selenium) in anhydrous benzene until one mol had been absorbed. The propylene was rapidly absorbed with heat evolution. The reaction mixture was allowed to stand for 24 hours in order that the second stage of the reaction might have ample time to be completed.

Theoretically, 48.15 g. or  $\frac{1}{4}$  of the selenium should be deposited in the two consecutive stages of the reaction; 45.5 g. was actually recovered. Upon evaporation of the filtrate a white crystalline product separated. The crude product was recrystallized from chloroform and dried at room temperature. *Bis*( $\beta$ -chloropropyl) selenide dichloride was obtained as white crystals melting at  $81^{\circ}$ .

*Analysis.* Calc. for  $C_4H_9Cl_2Se$ : Cl, 46.46. Found: 45.97.

*Bis(β-chlorobutyl) Selenide* was prepared by spraying a benzene solution of selenium monochloride into an atmosphere of butylene. Two hundred and fifteen cc. of selenium monochloride solution containing 68 g. of the monochloride (47 g. of selenium) was used, and 22.5 g. (calc. 23.5 g.) of selenium was recovered. The crude product obtained by evaporation of the solvent was submitted to distillation under reduced pressure. *Bis(β-chlorobutyl) selenide* was obtained as a yellow oil boiling at 138° under 8 mm. pressure. The product slowly darkens upon exposure to light.

*Analyses.* Calc. for  $C_8H_{16}Cl_2Se$ : Cl, 27.02. Found: 27.25, 27.29.

*Bis(β-chlorobutyl) Selenide Dichloride.*—In an attempt to prepare *bis(β-chlorobutyl) selenide dichloride*, 200 cc. of a benzene solution containing 64 g. of selenium monochloride (44 g. of selenium) was permitted to absorb an equimolecular quantity of dry butylene. The reaction mixture was allowed to stand for 24 hours and was then filtered. Instead of the calculated 33 g. ( $3/4$ ) only 26.5 g. of selenium was recovered as free selenium. The oily, crude product obtained upon evaporating the filtrate could not be induced to crystallize. It was decomposed by distillation even under strongly reduced pressure. After driving off the benzene as completely as possible, the crude product analyzed with the following results.

*Analyses.* Calc. for  $C_8H_{16}Cl_2Se$ : Cl, 42.57; calc. for  $C_8H_{16}Cl_4Se$ : Cl, 27.02. Found: 36.41, 36.64.

Both the chlorine content and the amount of selenium recovered indicate that the second stage of the reaction did not go to completion.

A solution of 15 g. of selenium monochloride (10.4 g. of selenium) in benzene was treated with an equimolecular quantity of *bis(β-chlorobutyl) selenide*. The reaction began immediately with the deposition of selenium. After standing for 24 hours at room temperature, the reaction mixture was filtered, whereupon 7 g. (calc. 10.4 g.) of selenium was recovered.

The chlorine content of the crude product is near that required for the unsymmetrical trichloro derivative, *β,β-dichloro-butyl-β'-chlorobutyl selenide*. That this product is not present in quantity, however, is evidenced by the fact that when the crude product is reduced in water solution with sulfur dioxide and the resulting oil dried and purified it distils at 138° under 8 mm. pressure, shows by analysis a chlorine content of 26.82% and is thus identical with *bis(β-chlorobutyl) selenide*.

*Bis(β-chloro-amy) Selenide.*—Since amylene is a liquid at room temperature, the operation in this case becomes quite simple. Thirty-five g. ( $1/2$  mol) of amylene was dissolved in 200 cc. of anhydrous benzene in the reaction chamber. A solution of 57.5 g. ( $1/4$  mol) of selenium monochloride in anhydrous benzene was added drop-wise with stirring. When the reaction was complete, the selenium was filtered off, washed with benzene and weighed. Of the 39.6 g. of selenium used, 19.5 g. was recovered as free selenium. The crude product obtained by evaporating the solvent was submitted to fractionation under diminished pressure. *Bis(β-chloro-amy) selenide* was obtained as a reddish-yellow oil boiling at 158° under 10 mm. pressure. The product cannot be completely distilled even under 10 mm. pressure with partial decomposition.

*Analyses.* Calc. for  $C_{10}H_{20}Cl_2Se$ : Cl, 24.41. Found: 23.92, 24.43.

*Bis(β-chloro-amy) Selenide Dichloride.*—In an attempt to prepare *bis(β-chloro-amy) selenide dichloride*, 35 g. ( $1/2$  mol) of amylene was gradually added to 115 g. ( $1/2$  mol) of selenium monochloride with stirring. Free selenium was deposited immediately. After standing for 24 hours, the reaction mixture was filtered, and 48 g. (calc. 59.7 g.) or  $3/4$  of the selenium was recovered. The chlorine content of the crude oil lay between that of the selenide and its dichloride.

*Analyses.* Calc. for  $C_{10}H_{20}Cl_2Se$ : Cl, 24.41; calc. for  $C_{10}H_{20}Cl_4Se$ : Cl, 39.27. Found: Cl, 29.44, 29.79.

By fractional distillation under diminished pressure there was obtained a quantity of reddish-yellow oil boiling at  $158^\circ$  under 10 mm. pressure. This product is doubtless unchanged *bis*( $\beta$ -chloro-amyl) selenide.

*Analyses.* Calc. for  $C_{10}H_{20}Cl_2Se$ : Cl, 24.41. Found: 24.97, 24.85.

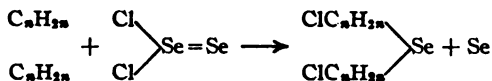
A solution of 15 g. of selenium monochloride in benzene was treated with a benzene solution of *bis*( $\beta$ -chloro-amyl) selenide in equimolecular quantities. Of the theoretical 10.4 g. of free selenium, 6 g. was recovered.

### Discussion of Results.

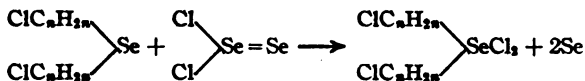
The above results demonstrate beyond question that the relation between the two products described for a given olefin is the same as that of alkyl selenide and corresponding alkyl selenide dichloride. The equation used to explain the mechanism of their formation will depend upon the structure accepted for selenium monochloride. The structure most adaptable is that suggested by Konek-Norwall<sup>7</sup> which represents it as unsymmetrical di-

chloro-diselenide  $\begin{array}{c} Cl \\ \diagup \\ Cl \end{array} Se = Se$ . In fact, the authors believe the results obtained in the syntheses described above to be strong evidence of the correctness of the unsymmetrical structure of selenium monochloride.

Using the unsymmetrical structure for selenium monochloride, the absorption of olefins may be expressed as follows.

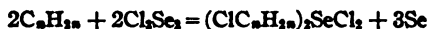


This is the first stage of the reaction and represents what takes place when selenium monochloride is brought into an excess of the olefin. The conversion of alkyl selenides into their dichlorides by direct chlorination or by further reaction with active chlorides is a well-known reaction.<sup>8</sup> This accounts for the second stage of the reaction which takes place when the olefin is led directly into selenium monochloride solution.



The simple selenide first formed is converted by the excess of selenium monochloride into the selenide dichloride, setting free 2 additional atoms of selenium.

The summation of these two equations is analogous to that given by Pope and his co-workers.<sup>3</sup>

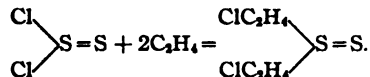


<sup>7</sup> Konek-Norwall, *Oesterr. Chem. Zig.*, 16, 288 (1913).

<sup>8</sup> Joy, *Ann.*, 86, 35 (1853). Jackson, *ibid.*, 179, 1 (1875).

### The Chemistry of the Formation of Mustard Gas.

The chemistry involved in the preparation and properties of the selenium derivatives is of interest, further, in the light it sheds upon the formation of the mustard gas from sulfur monochloride. Accepting an analogous structure for sulfur monochloride the absorption of ethylene may be expressed



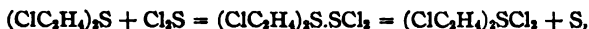
In this case the persulfide sulfur atom being more like chlorine does not always split off spontaneously. This structure, which has already been suggested by Green,<sup>9</sup> readily accounts for the formation of mustard gas polysulfides, the existence of which has been so clearly demonstrated by Conant, Hartshorn and Richardson.<sup>10</sup> The mechanism of this polysulfide formation is probably quite analogous to that by which hypochlorites are converted into chlorates.



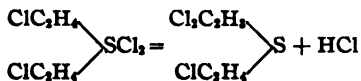
The tendency of sulfur and selenium to seek a higher valence when in the form of their alkyl derivatives may also be an explanation of the fact observed by Conant, Hartshorn and Richardson that the chlorides of sulfur, particularly the dichlorides, rapidly absorb only one molecular quantity of ethylene, when ethylene is led into the sulfur chloride solution.



or



the hypothetical mustard gas dichloride undergoing spontaneous decomposition with the evolution of hydrogen chloride and the simultaneous formation of the trichloro derivative.



In this connection it is interesting to note the observations of Williams,<sup>11</sup> who says: "It is essential that the reaction between ethylene and sulfur monochloride be completed in the minimum possible time," and also of Gibson and Pope,<sup>12</sup> who state: "The sulfur dichloride method is difficult to control, because  $\beta, \beta'$ -dichloro-ethyl sulfide is acted on rapidly by sulfur dichloride; it is necessary that little or no sulfur dichloride remain long in contact with the  $\beta, \beta'$ -dichloro-ethyl sulfide produced." Meyers<sup>13</sup> has

<sup>9</sup> Green, *J. Soc. Chem. Ind.*, **38**, 469R (1919).

<sup>10</sup> Conant, Hartshorn and Richardson, *THIS JOURNAL*, **42**, 585 (1920).

<sup>11</sup> Williams, *J. Soc. Chem. Ind.*, **38**, 451R (1919).

<sup>12</sup> Gibson and Pope, *J. Chem. Soc.*, **117**, 271 (1920).

<sup>13</sup> Meyers, *J. Soc. Chem. Ind.*, **39**, 65T (1920).

reported that by spraying sulfur dichloride into an atmosphere of ethylene he was able to obtain mustard gas of 93% purity after one distillation.

### Summary.

1. The reaction between selenium monochloride and olefins is shown to take place in two stages.

2. By spraying the monochloride or its solution into an atmosphere of olefin the reaction may be stopped at the first stage. In this manner *bis*-( $\beta$ -chloropropyl) selenide, *bis*-( $\beta$ -chlorobutyl) selenide, and *bis*-( $\beta$ -chloroamyl) selenide have been prepared, and their properties described.

3. By leading the olefin into selenium monochloride or its solution the above products are acted upon by the excess of the monochloride, being converted into *bis*-( $\beta$ -chloropropyl) selenide dichloride, *bis*-( $\beta$ -chlorobutyl) selenide and *bis*-( $\beta$ -chloroamyl) selenide dichloride, respectively. This constitutes the second stage of the reaction.

4. The mechanism of the reaction between selenium monochloride and olefins is formulated, using the unsymmetrical structure for selenium monochloride. The quantitative results obtained in these syntheses is offered as evidence in favor of the unsymmetrical structure for selenium monochloride.

5. The same mechanism has been applied to explain the formation of mustard gas from ethylene and sulfur monochloride. The possibility of preparing mustard gas by spraying sulfur monochloride is again pointed out.

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[CONTRIBUTION FROM THE CARBOHYDRATE LABORATORY, BUREAU OF CHEMISTRY,  
U. S. DEPARTMENT OF AGRICULTURE.]

## CRYSTALLINE CHLORO-TETRA-ACETYL MANNOSE.

BY D. H. BRAUNS.

Received November 25, 1921.

A halogenated derivative of an acetylated sugar was first obtained by Colley<sup>1</sup> by the action of acetyl chloride on glucose in a sealed tube at room temperature. The author, however, succeeded only twice in crystallizing the syrupy chloro-tetra-acetyl glucose. As this derivative was found to be a valuable intermediate for preparing synthetic glucosides,<sup>2</sup> many chemists have studied different methods for preparing crystalline halogenated acetyl derivatives of sugars. Koenigs and Knorr<sup>3</sup> prepared bromo-acetyl glucose in a crystalline condition by shaking glucose with acetyl bromide at ordinary temperature, the derivative separating from the

<sup>1</sup> Colley, *Ann. chim. phys.*, [4] 21, 367 (1870).

<sup>2</sup> Michael, *Am. Chem. J.*, 1, 305 (1879).

<sup>3</sup> Koenigs and Knorr, *Ber.*, 34, 957 (1901).

concentrated, washed and dried ether solution. This method was successfully simplified by Moll van Charante,<sup>4</sup> who found that shaking was not necessary.

More recent investigators successfully used the fully acetylated sugar as an intermediate. Von Arlt<sup>5</sup> obtained crystalline chloro-acetyl glucose by the action of phosphorus pentachloride and aluminum chloride on a solution of penta-acetyl glucose in chloroform. Bodart<sup>6</sup> prepared crystalline chloro-acetyl lactose by suspending lactose in acetic anhydride and passing hydrogen chloride into the mixture. Skraup and Koenig<sup>7</sup> used Bodart's method on cellulose, obtaining crystalline chloro-acetyl cellulose. Fischer and Armstrong<sup>8</sup> used dry hydrogen chloride, acetyl chloride and hydrobromic acid on the fully acetylated sugar under high pressure at room temperature, and obtained in this way crystalline chloro- and bromo-acetyl glucose, as well as crystalline chloro-acetyl galactose and chloro-acetyl maltose. Ryan and Mills<sup>9</sup> prepared crystalline chloro-acetyl arabinose by the action of acetyl chloride on arabinose in an open vessel. Crystalline chloro-acetyl xylose was obtained by Ryan and Ebrill<sup>10</sup> by treating xylose with acetyl chloride at 0°. The corresponding crystalline bromo-acetyl xylose has also been prepared<sup>11</sup> by the action of a concentrated solution of hydrobromic acid in acetic anhydride on xylose. E. Fischer and H. Fischer<sup>12</sup> have devised a method for preparing bromo-acetyl lactose by the action of a saturated solution of hydrobromic acid in glacial acetic acid on octa-acetyl lactose at room temperature, no sealing of the vessel being necessary. This method was recognized as one of the simplest ways to obtain the reactive bromo-acetyl derivatives of many sugars, and crystalline bromo-acetyl rhamnose was prepared.<sup>13</sup> The procedure for the preparation of bromo-acetyl glucose<sup>14</sup> was described in detail and the possibility of preparing the earlier reported  $\alpha$  halogenated derivatives of the sugars according to any description of their preparation was denied, as all the described methods yielded the  $\beta$  halogenated derivatives of the sugars. These earlier reported  $\alpha$  derivatives are also

<sup>4</sup> Moll van Charante, *Rec. trav. chim.*, 21, 42 (1902).

<sup>5</sup> Von Arlt, *Monatsh.*, 22, 144 (1901). See also Skraup and Kremann, *ibid.*, 22, 373 (1901).

<sup>6</sup> Bodart, *ibid.*, 22, 1033 (1901); 23, 1 (1902).

<sup>7</sup> Skraup and Koenig, *ibid.*, 22, 1033 (1901).

<sup>8</sup> Fischer and Armstrong, *Ber.*, 34, 2885 (1901).

<sup>9</sup> Ryan and Mills, *J. Chem. Soc.*, 79, 704 (1901).

<sup>10</sup> Ryan and Ebrill, *Proc. Roy. Dublin Soc.*, 11, 249 (1903-8). See also Hudson and Johnson, *THIS JOURNAL*, 37, 2751 (1915).

<sup>11</sup> Dale, *THIS JOURNAL*, 37, 2745 (1915). See also Hudson and Johnson, *Ref. 10*.

<sup>12</sup> E. Fischer and H. Fischer, *Ber.*, 43, 2530 (1910).

<sup>13</sup> Fischer and Oetker, *ibid.*, 46, 4035 (1913). See also Fischer, Bergmann and Rabe, *ibid.*, 53, 2370 (1920).

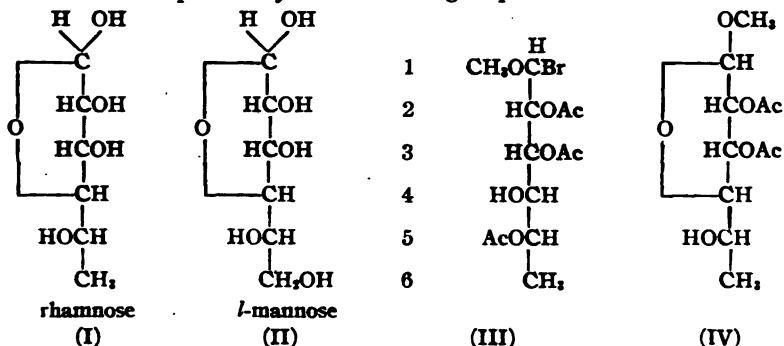
<sup>14</sup> Fischer, *ibid.*, 44, 1903 (1911).

given in several handbooks. Crystalline  $\alpha$ - and  $\beta$ -chloro-tetra-acetyl fructose have, however, been prepared.<sup>16</sup>

This introductory study of the literature discloses that *mannose* is the only readily available sugar from which a crystalline halogenated acetyl derivative has not yet been prepared. Non-reducing sugars, as sucrose, need not be considered, as they do not contain a labile hydroxyl group easily replaceable by halogen. Fischer and Hirschberger<sup>16</sup> in 1889 applied Colley's method to mannose by shaking this sugar with 5 parts of acetyl chloride, and obtained a syrupy chloro-tetra-acetyl mannose with properties analogous to those of the syrupy chloro-tetra-acetyl glucose of Colley. Later Fischer and Oetker<sup>17</sup> succeeded in obtaining  $\beta$ -penta-acetyl mannose in a crystalline state by acetylating with certain precautions. They tried Fischer's bromination method on this crystalline compound, using a saturated solution of hydrobromic acid in glacial acetic acid but were not successful in crystallizing the syrupy bromo-acetyl mannose.

### Theoretical Considerations.

By applying the method of von Arlt<sup>8</sup> with some important modifications, fully described in the following pages, it has been possible to prepare crystalline chloro-tetra-acetyl mannose, and to open the way for the preparation of several derivatives of this sugar. The behavior of the halogenated tetra-acetyl derivative of mannose toward methyl alcohol and silver carbonate (reaction of Koenigs and Knorr) promises to be of special interest on account of the analogy in the structures of mannose and rhamnose. These two sugars differ only in that the methyl group in rhamnose is replaced by the  $\text{CH}_2\text{OH}$  group in mannose.



The interesting results obtained by Fischer, Bergmann and Rabe<sup>18</sup> have

<sup>16</sup> Brauns, *THIS JOURNAL*, 42, 1846 (1920). See also Jaeger, *Verslag. Akad. Wetenschappen Amsterdam*, 29, 150 (1920).

<sup>17</sup> Fischer and Hirschberger, *Ber.*, 22, 3224 (1889).

<sup>18</sup> Fischer and Oetker, *Ref. 13*. See also Hudson and Dale, *THIS JOURNAL*, 37, 1280 (1915).

<sup>19</sup> *Ref. 13*.



established the fact that the reaction of Koenigs and Knorr applied to crystalline bromo-tetra-acetyl rhamnose yields a mixture of 3 *different methyl tri-acetyl rhamnoses*, notwithstanding the results of several experiments which showed that crystalline bromo-tri-acetyl rhamnose is not a mixture but one chemical individual. This peculiar behavior can be explained only in the following way. First, addition of methyl alcohol takes place by breaking the oxygen ring, the available new valences being saturated by  $\text{CH}_3\text{O}$  and  $(\text{O})\text{H}$  groups (III). This substance splits off hydrogen bromide in the 4-1 position, by which ordinary  $\beta$  methyl tri-acetyl rhamnose is formed (IV). At the same time the addition product undergoes intermolecular rearrangement by which the hydrogen of the hydroxyl group in the position changes place with the acetyl group in the third *or* the fifth position, which ultimately leads to the formation of two other methyl tri-acetyl rhamnoses, having their oxygen ring formation in the 1-3 *or* the 1-5 position. This explains the formation of the 3 methyl tri-acetyl rhamnoses. One of these three compounds loses only 2 acetyl groups on alkaline hydrolysis. The third acetyl group is removed only on acid hydrolysis, a peculiarity which is well explained by its formula, as the 1-3 position of the oxygen ring protects one acetyl group. This behavior of bromo-acetyl rhamnose differs from that of chloro- or bromo-tetra-acetyl *glucose* and *galactose* which yield only one derivative each, the  $\beta$ -methyl tetra-acetyl derivative, having the oxygen ring formation in the 1-4 position. This behavior, however, as will be reported in detail later, resembles that of the crystalline chloro-tetra-acetyl mannose, which also gives a mixture of various methyl tetra-acetyl mannoses, in spite of the fact that crystalline chloro-tetra-acetyl mannose is a pure substance, not a mixture.

### Experimental Work.

Crystalline  $\beta$ -penta-acetyl mannose was obtained by acetylating  $\beta$ -mannose at  $0^\circ$  with acetic anhydride and zinc chloride.<sup>19</sup> This penta-acetyl mannose was converted into chloro-tetra-acetyl mannose by applying, with certain modifications, the method which von Arlt<sup>6</sup> used for preparing chloro-acetyl glucose. It is especially important that ether must not be used, and that the reaction product be freed as completely as possible from chloroform before petroleum ether is added.

**Method of Preparation.**—Fifteen g. of crystalline  $\beta$ -penta-acetyl mannose was dissolved in 30 cc. of dry chloroform in an Erlenmeyer flask with glass stopper, and 4 g. of dry (sublimed) aluminum chloride and 9 g. phosphorus pentachloride added. The mixture was slightly warmed on the steam-bath in order to keep the reaction going slowly, shaking not being necessary. After  $\frac{1}{2}$  to 1 hour, in which nearly all of the aluminum chloride and phosphorus pentachloride had disappeared forming a greenish solution, the reaction product was cooled and thoroughly shaken in a separatory funnel with ice-

<sup>19</sup> Hudson and Dale, Ref. 17.

water and pieces of ice. The watery solution was drawn off and the shaking with ice-water repeated thrice. The watery solution may be shaken again with chloroform, and the chloroform extract added to the main part before a new portion of ice-water is added. The chloroform solution was dried with anhydrous sodium sulfate, evaporated *in vacuo*, and the resulting solution heated on the steam-bath at moderate temperature with constant stirring until the chloroform was evaporated as completely as possible. The syrupy residue may be dried in a vacuum desiccator in order to remove traces of chloroform. The dry, colorless residue was stirred with a small amount of petroleum ether, and the sides and bottom of the crystallizing dish scratched. If crystallization does not occur, the petroleum ether may be poured off and replaced by a little fresh petroleum ether and the mixture cooled and stirred. After crystallization had started, the whole mass solidified and no difficulty was encountered in crystallizing subsequent preparations. For recrystallizing, the nearly pure product was reduced to a fine powder, boiled with 100 cc. of petroleum ether (b. p. 30–35°), and the boiling solution rapidly filtered through a folded filter into a beaker. This solution was kept separate, as it contained most of the impurities. The extraction was repeated 4 times with 200 cc. of petroleum ether. By evaporating the petroleum ether in the air (in the hood) beautiful, brilliant crystals were deposited. These were found to be pure chloro-tetra-acetyl mannose, as repeated fractional crystallization did not change the melting point or specific rotation. The yield was about 9 g., or 64% of the calculated amount.

**Identification and Properties.**—Combustion with lead chromate gave the following results.

Subs., 0.2412, 0.2427:  $\text{CO}_2$ , 0.4033, 0.4065;  $\text{H}_2\text{O}$ , 0.1136, 0.1167. Calc. for  $\text{C}_6\text{H}_7\text{O}(\text{C}_2\text{H}_3\text{O}_2)_4\text{Cl}$ : C, 45.83; H, 5.22. Found: C, 45.61, 45.68; H, 5.27, 5.38.

A chlorine determination on the original substance gave the following data. Subs. 0.2196:  $\text{AgCl}$  (Carius), 0.0847. Calc. for  $\text{C}_6\text{H}_7\text{O}(\text{C}_2\text{H}_3\text{O}_2)_4\text{Cl}$ : Cl, 9.67. Found: 9.54.

The quantitative estimation of acetyl was combined with the quantitative estimation of chlorine by the following method. 0.6000 g. of finely powdered substance was saponified by shaking with 181.3 cc. of 0.1 *N* sodium hydroxide solution for 7 hours at 0° and titrating with 0.1 *N* sulfuric acid and phenolphthalein. For neutralization 99.1 cc. of 0.1 *N* sulfuric acid was required; hence 82.2 cc. of 0.1 *N* sodium hydroxide had been neutralized. An excess of silver nitrate solution was added to the warm neutral solution and the precipitate filtered on a weighed Gooch crucible. 0.2340 g. of silver chloride, equivalent to 9.65% of the chlorine in the substance, was obtained. The 0.2340 g. of silver chloride had been formed from an amount of hydrochloric acid corresponding to 16.3 cc. of 0.1 *N* hydrochloric acid; hence in 0.6000 g. of substance  $82.2 - 65.3 = 65.9$  cc. of 0.1 *N* solution, or 65.9% acetic acid, was found. In a similar experiment, 9.61% of chlorine and 65.9% of acetic acid were found. The theoretical quantities for chloro-tetra-acetyl mannose are 9.67% of chlorine and 65.5% of acetic acid.

For identifying the preparation as a mannose derivative, the liquids resulting from these estimations were concentrated and filtered, and a concentrated solution of 0.7 g. of phenylhydrazine in dil. acetic acid was added. After standing for a short time, the separated hydrazone was filtered off and washed with ice-water, alcohol and ether. The yield was 0.6 g. of pure mannose phenylhydrazone, identified by its melting point. Since no particular precautions were taken for obtaining quantitative results, it may be mentioned that 0.9 g. of mannose phenylhydrazone is the theoretical amount obtainable from 1.2 g. of chloro-tetra-acetyl mannose. A small amount of crystalline mannose, identified by its melting point and specific rotation, was also obtained by boiling chloro-tetra-acetyl mannose for 5 hours under a reflux condenser with 0.1 *N* sulfuric acid, precipitating the sulfuric acid and hydrochloric acid with barium hydroxide and silver

acetate, and extracting the concentrated filtrate with absolute alcohol. Crystalline mannose separated on evaporating the alcohol in a vacuum desiccator.

The molecular weight of chloro-tetra-acetyl mannose was determined by the lowering of the freezing point of benzene. In three experiments, 3.8864, 6.6319 and 8.2938 g. of substance per 100 g. of benzene gave the respective depressions  $0.523^{\circ}$ ,  $0.890^{\circ}$  and  $1.090^{\circ}$ , from which the values 370, 372 and 390 are obtained for the molecular weight in comparison with the theoretical value 367.

The specific rotation was measured in chloroform solution. 1.1497 g. of once recrystallized chloro-tetra-acetyl mannose was made up to 25 cc. with U. S. P. chloroform. The rotation, measured in a 2dcm. tube at  $20^{\circ}$  with sodium light, was 8.18 circular degrees to the right; hence  $[\alpha]_D^{20} = +88.9$ . After a second recrystallization from petroleum ether, 1.4038 g. of substance made up to 25 cc. with chloroform produced a rotation in a 2dcm. tube of 10.068 circular degrees to the right; hence  $[\alpha]_D^{20} = 89.64$ . After a third recrystallization from petroleum ether, 1.0358 g. of substance made up to 25 cc. with chloroform produced a rotation in a 2dcm. tube of 7.416 circular degrees to the right; hence  $[\alpha]_D^{20} = +89.50$ , which is taken as the specific rotation of the pure substance. Chloro-tetra-acetyl mannose is a stable substance, as it was kept in a desiccator during the hot summer months without decomposition. The melting point is  $81^{\circ}$ . It is colorless and odorless, has a bitter taste and is very soluble in the usual solvents other than water and petroleum ether.

### Summary.

Chloro-tetra-acetyl mannose, hitherto known only in the form of a syrup, has been obtained in crystalline form.

The behavior of the crystalline substance toward methyl alcohol and silver carbonate (reaction of Koenigs and Knorr) is analogous to that of bromo-tri-acetyl rhamnose. This is well accounted for by their structural formulas given in this paper.

In the case of chloro-tetra-acetyl mannose, this reaction leads to various methyl tetra-acetyl derivatives and in this respect chloro-tetra-acetyl mannose differs from the corresponding derivatives of glucose and galactose, which yield only one methyl tetra-acetyl derivative.

This difference in behavior may lead to a more detailed knowledge of the arrangement of the constituent parts of their molecules.

WASHINGTON, D. C.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF PRINCETON UNIVERSITY.]

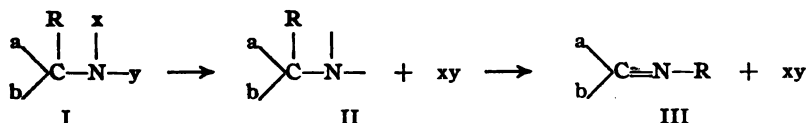
# NEW HYDROXAMIC ACIDS DERIVED FROM CYCLOPROPANE CARBOXYLIC ACID, ISOBUTYRIC ACID AND DIBENZYL-ACETIC ACID. A COMPARATIVE STUDY OF THE BECKMANN REARRANGEMENT OF THEIR DERIVATIVES.<sup>1</sup>

BY LAUDER WILLIAM JONES AND ALFRED W. SCOTT.

Received December 1, 1921.

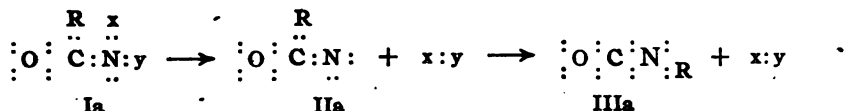
## I. Introduction.

Although many different classes of organic compounds show rearrangements of the Beckmann<sup>2</sup> type, there is one fundamental transformation which stands out as essential to all such reactions; some radical, R, attached to a carbon atom in the original compound, is found in combination with a nitrogen atom after the rearrangement has occurred. If oximes are excluded, a general formula may be employed to represent the classes of compounds which show such changes.



The symbols a and b stand for R<sub>2</sub>, O=, HN=, and for similar groups; while x and y may be replaced by H or a metal atom together with some other radical such as Cl, Br, OH, OCOR. In the azides, N<sub>3</sub>= takes the place of x and y.

For several years, plain structural formulas of this kind have been replaced by electronic formulas<sup>3</sup> in which positive and negative signs serve to represent bonds between atoms. In an article<sup>4</sup> recently published in THIS JOURNAL, the rearrangement of a hydroxamic acid derivative was represented by symbols more in harmony with recent views concerning the structure of the atom and the nature of "bonds" in organic compounds. Thus:



<sup>1</sup> This article is based upon a thesis submitted by Alfred W. Scott to the Faculty of the Graduate School of Princeton University in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

<sup>2</sup> In this article, the term Beckmann rearrangement is used in its broadest sense and includes rearrangements of the Hofmann, of the Curtius and of the Lossen types.

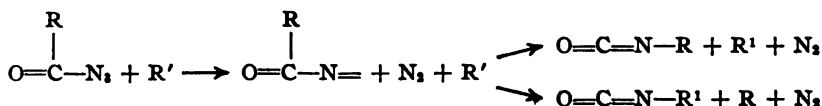
<sup>3</sup> Jones, *Am. Chem. J.*, 48, 25 (1921); 50, 441 (1913); THIS JOURNAL, 36, 1268 (1914). Stieglitz, *ibid.*, 36, 288 (1914).

<sup>4</sup> Jones and Hurd, THIS JOURNAL, 43, 2424 (1921).

It has been assumed for some time that, during the reaction, the radical R separates from the carbon atom and "wanders" to the univalent nitrogen atom (IIa) not because of "any complicated mechanism" such as ring formation, a bivalent carbon radical, or the like,<sup>5</sup> but, rather, under the influence of electrical constraint brought about by the necessity for redistribution of electrons<sup>3</sup> to form the more stable system represented by the isocyanate stage (IIIa) in the reaction.

If this be the case, then, while the positive radical R is shifting its position from the carbon atom to the nitrogen atom, it must exist momentarily as a *free radical*. An hypothesis which follows logically as a consequence of this conclusion was advanced in the article mentioned above;<sup>4</sup> *viz.*, that an intimate relation must exist between the ease of rearrangement of the univalent nitrogen derivative (IIa) and the ability of the radical R to exist as a *free radical* (e. g., triphenylmethyl, tri-biphenylmethyl, etc.).

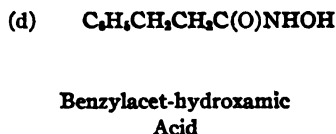
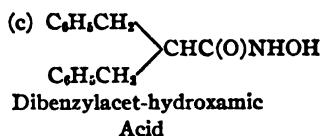
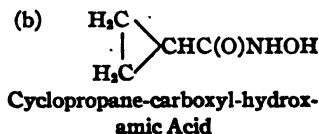
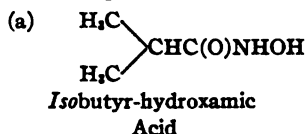
Furthermore, this assumption suggests definite experiments which are now being tried in this laboratory. If certain azides,  $RCON_3$ , are caused to undergo rearrangement in a solution which contains a group such as triphenylmethyl, it seems probable that *this free radical* may compete with the radical R for possession of the nitrogen position and, consequently, that *two isocyanates may be formed* instead of one.



Thus, with benzoyl azide,  $C_6H_5CON_3$ , and triphenylmethyl, both phenyl isocyanate and triphenylmethyl isocyanate would be expected. The results of these experiments will be published later.

The compounds described in this paper were prepared and studied for the purpose of determining the influence which certain hydrocarbon radicals would exert in producing variations in the ease of rearrangement of several related hydroxamic acid derivatives.

For this purpose, the following series of hydroxamic acids was prepared. With the exception of (d), the parent substances were new compounds.



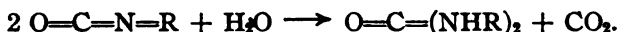
<sup>5</sup> Stieglitz (Hesse), *Am. Chem. J.*, 29, 57 (1903). Nef, *Ann.*, 298, 308 (1897); 318 (1901). Jones, Ref. 3.

Compound (d) was studied by Thiele and Pickard<sup>6</sup> and the behavior of some of its derivatives described. This acid was included in the series in order to be able by comparison to determine more definitely the effect of the second benzyl group in Compound (c).

The preparation of tribenzylacetic acid was undertaken in order to note the effect of three benzyl groups. For this purpose, tribenzylmethyl chloride was synthesized. However, since this chloride failed to react to give a Grignard reagent, we have not synthesized tribenzylacetic acid; so the study of tribenzylacet-hydroxamic acid and its derivatives was discontinued for the present.

The reactions of the potassium, sodium, and silver salts of the acetyl esters and of the benzoyl esters of the parent substances were used for comparison. Dry salts of this kind usually have a fairly definite temperature at which they puff or explode to form an isocyanate and an acetate or benzoate. However, the length of time the salts have been kept after their preparation frequently alters perceptibly the temperature at which this change occurs.

In order to avail ourselves of a somewhat more reliable source of information concerning the ease of rearrangement of these salts, the effect of heat upon clear aqueous solutions of the potassium and the sodium salts was also studied. Under these circumstances, the isocyanate first produced is usually converted into the corresponding *sym*.di-substituted urea



## II. Comparison and Interpretation of Results.

The following table shows the temperatures at which sudden decomposition of the dry salts occurred.

TABLE I  
DECOMPOSITION TEMPERATURES

Parent hydroxamic acids	Benzoyl Ester			Acetyl Ester		
	K Salt	Na Salt	Ag Salt	K Salt	Na Salt	Ag Salt
(CH <sub>3</sub> ) <sub>2</sub> CHCONHOH (a)	Spontaneous	75°	Above 200°	Spontaneous	—	—
(C <sub>6</sub> H <sub>5</sub> )CONHOH (b)	103°	143°	Above 200°	155°	—	—
(C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> ) <sub>2</sub> CHCONHOH (c)	Not isolated	Not isolated	143°	Not isolated	Not isolated	145°

These substances may be regarded as derivatives of acet-hydroxamic acid. On the other hand, Compounds (b) and (c) bear a structural relation to *isobutyryl*-hydroxamic acid (a).

<sup>6</sup> Thiele and Pickard, *Ann.*, 309, 197 (1921).

In the interpretation of this table, we shall make the assumption that extreme ease of rearrangement explains the failure to isolate some of the salts of (c). No doubt, the failure to obtain these salts may be attributed, in part, to their solubility in alcohol-ether in which they were prepared. From a general survey of the table, it appears that, in every case, the derivatives of (c) were found to undergo rearrangement with the greatest ease; that the compounds of (b) required the highest temperature to effect their rearrangement; and that the salts of (a) occupy an intermediate position. It is interesting to note, that, in the case of the salts of each hydroxamic acid ester (dihydroxamic acid) the ease of rearrangement was as follows:  $K > Na > Ag$ .

Two salts, both derivatives of (a), exhibited properties worthy of special mention. A pure sample of the potassium salt of the benzoyl ester of *isobutyryl*-hydroxamic acid was made and placed in a desiccator. The desiccator was evacuated, and in less than 20 minutes the salt decomposed spontaneously with such violence as to scatter potassium benzoate throughout the entire container.

The potassium salt of the acetyl ester of (a) exhibited the same phenomenon, although, in this instance, it was necessary for the salt to stand in an evacuated desiccator from 5 to 6 hours before the change occurred. Two similar cases have been described previously; *viz.*, the potassium salt of the benzoyl ester of phenylacet-hydroxamic acid<sup>7</sup> and the sodium salt of the benzoyl ester of dichloro-acet-hydroxamic acid.<sup>8</sup>

In studying the second method of comparison of the different salts given in Table I, it was found that the temperature required to produce a precipitate in an aqueous solution of the potassium salt, also caused a precipitate with an aqueous solution of the sodium salt of the same hydroxamic acid ester. Therefore, the table given in Table II was condensed in order that the behavior of these compounds could be seen at a glance.

Rearrangement was determined by measuring the temperature at which clear aqueous solutions (approximately equivalent) of the salts of alkali metals began to give a precipitate. The components of the precipitate were determined. In the case of the cyclopropane series, about 75% of the corresponding hydroxamic ester was found to be regenerated. The presence of this proportion of the ester showed that, to a large extent, simply hydrolysis of the salt had taken place, and that rearrangement to give the isocyanate and then the urea was distinctly a secondary reaction. In the *isobutyric* acid series, similar products of hydrolysis were also detected; here, however, the urea was the primary product and the regenerated ester occurred in almost negligible amounts. A more detailed

<sup>7</sup> Jones, *Am. Chem. J.*, **48**, 8 (1912).

<sup>8</sup> Jones and Sneed, *THIS JOURNAL*, **39**, 670 (1917).

description of the treatment to which these salts were subjected will be found in the experimental part. The temperatures recorded in the table are those of the bath employed in heating the vessel which contained the different solutions.

TABLE II

Parent Hydroxamic Acids	Aqueous Solutions of the Potassium or Sodium Salts of the Benzoyl Esters
	° C.
(CH <sub>3</sub> ) <sub>3</sub> CHCONHOH	(a) 50 chiefly rearrangement
(C <sub>2</sub> H <sub>5</sub> )CHCONHOH	(b) 90 mainly hydrolysis
(C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> ) <sub>2</sub> CHCONHOH	(c) 20 rearrangement
(C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> )CH <sub>2</sub> CONHOH	(d) 80 rearrangement

It may be seen that, insofar as the ease of arrangement is concerned, the results of this table agree fairly well with those of Table I. Since the acyl group was always the same (*viz.*, benzoyl) and, from Table II, we see that the metal atom caused no appreciable difference in reactivity, we are forced to the conclusion that the variations in behavior of these compounds must be attributed to the influence of the hydrocarbon radicals of the acyl groups from which the hydroxamic acids were originally formed. Therefore, in terms of these radicals the ease of rearrangement may be expressed by the following sequence: dibenzylmethyl > *isopropyl* > benzylmethyl > cyclopropyl.

Without further consideration, it can be seen that, among these hydroxamic acid derivatives, those which contain the trimethylene ring are the most stable. On the other hand, the derivatives of *isobutyryl*-hydroxamic acid show a remarkable tendency to rearrange. This is especially noteworthy, because of the intimate structural relationship which exists between the hydroxamic acids derived from *isobutyric* acid, and the corresponding derivatives of cyclopropane-monocarboxylic acid.



It may be noted also that derivatives of acet-hydroxamic acid<sup>9</sup> and of propionhydroxamic acid<sup>10</sup> undergo rearrangement with greater difficulty than the corresponding derivatives of *isobutyryl*-hydroxamic acid.

The wide differences observed in the behavior of derivatives of benzylacetic acid and of dibenzylacetic acid seems, at first, to lead to the assumption that the introduction of the second benzyl radical increases, in a marked degree, the ease with which corresponding derivatives undergo

<sup>9</sup> Jones, *Am. Chem. J.*, 29, 1 (1898).

<sup>10</sup> The benzoyl ester of propionhydroxamic acid was prepared by Jones and Neuffer, *THIS JOURNAL*, 39, 664 (1917). It was observed that the solid potassium salt of this ester decomposed at 120–124°, the sodium salt, at 86° and the silver salt, above 150°.



rearrangement. However, the fact that derivatives of acethydroxamic acid<sup>9</sup> and of propionhydroxamic acid<sup>10</sup> (methylacet-hydroxamic acid) are not so sensitive to rearrangement as similar derivatives of *isobuty*-hydroxamic acid (dimethylacet-hydroxamic acid) seems to force upon us the conclusion that at least a part of the effect produced by the introduction of the second benzyl radical must be attributed to the formation of an *iso*- or branched chain.

The relations existing between chemical constitution and melting points are presented in the following table.

Parent Hydroxamic Acids	°C.	Benzoyl Ester	°C.	Acetyl Ester	°C.
(CH <sub>3</sub> ) <sub>2</sub> CHCONHOH	(a) 116	148		87	
(C <sub>6</sub> H <sub>5</sub> )CHCONHOH	(b) 112	150		108	
(C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> ) <sub>2</sub> CHHONHOH	(c) 146	147		126	

It is interesting to note that the difference between the melting points of dibenzylacet-hydroxamic acid and of its benzoyl ester is only one degree. A regularity is observed throughout the series, *viz.*, the melting points of the free hydroxamic acids lie between those of the higher-melting benzoyl derivatives and of the lower-melting acetyl derivatives.

### III. Consideration of Some Details.

The behavior of cyclopropane-monocarboxyl-hydroxamic acid and its derivatives was of particular interest, since no other hydroxamic acids related to cyclic hydrocarbons other than benzene and its homologs, or hydrocarbons with condensed benzene nuclei, have ever been described.

In the preparation of this hydroxamic acid, the method employed by Perkin<sup>11</sup> for the preparation of the necessary ethyl cyclopropane-monocarboxylate was found to give the best results. However, by modifying Perkin's procedure in several details, we have been able to obtain yields 50% better than those secured by him.

It was observed that the formation of dibenzylacet-hydroxamic acid by the interaction of ethyl dibenzylacetate and free hydroxylamine proceeded very slowly, even when the reaction mixture was kept between 60° and 70°. The presence of an extra mol of sodium methylate failed to increase the speed of the reaction to any great extent.

It was found that this hydroxamic acid could be prepared readily and in quantity by the action of free hydroxylamine on the acid chloride dissolved in benzene. The preparation of hydroxamic acids from acid chlorides is a well known method.<sup>12</sup> If water, generally employed, is used as the reaction medium, a mixture of the mono- and the dihydroxamic acids always results. The method suggested above for obtaining mono-

<sup>11</sup> Perkin, *J. Chem. Soc.*, **75**, 921 (1899).

<sup>12</sup> Lossen, *Ann.*, **161**, 347 (1872); **175**, 285 (1875).

hydroxamic acids gives yields almost quantitative, with no traces of the di-acids; it has been studied previously in this laboratory.<sup>4</sup>

### Experimental Part.

#### 1. Hydroxamic Acids Related to Cyclopropane Carboxylic Acid.

**The Preparation of Ethyl Cyclopropane-1:1-Cyanocarboxylate.**—Perkin<sup>13</sup> described the preparation of cyclopropane-monocarboxylic acid in which an alcoholic solution of sodium ethyl malonate and ethylene dibromide was digested under pressure. All attempts to prepare the acid by this method gave very small yields. Later Perkin<sup>14</sup> stated that when ethyl cyano-acetate was substituted for ethyl malonate and the mixture was digested at ordinary pressure, he was able to obtain a 50% yield of ethyl cyclopropane-1:1-cyanocarboxylate. We found the latter method preferable.

The changes made in Perkin's synthesis consisted first, in the use of an automatic stirrer; and second, in the elimination of the washing to which Perkin submitted the product of reaction to remove colored materials. We find that practically all the color is eliminated by the steam distillation which follows.

To 400 cc. of absolute alcohol in a flask provided with an automatic stirrer and reflux condenser, 27.4 g. of sodium was added in small portions. After all of the sodium had disappeared and the solution had cooled to room temperature, 100 g. of ethyl cyano-acetate was introduced; this caused the sodium salt to separate. Then 100 g. of ethylene dibromide was introduced and the mixture was heated to boiling on a water-bath. The reaction mixture was stirred continuously during the entire operation. After the product had become neutral to litmus, all of the alcohol was distilled and sufficient water was added to dissolve the sodium bromide which had separated. The mixture was extracted with ether several times, the ether was evaporated, and the residual oil was submitted to steam distillation. This distillate was saturated with ammonium sulfate and extracted with ether 5 or 6 times. After the ether had been dried over calcium chloride, it was distilled and the oil was submitted to fractional distillation. The distillate which boiled between 212° and 216°, weighed 64.4 g. Yield, 76%.

**The Preparation of 1:1-Cyclopropane-dicarboxylic Acid** was carried out according to the method described by Perkin. A portion of the acid, recrystallized from ether, gave a melting point of 134°.

**The Preparation of Cyclopropane-monocarboxylic Acid.**—In the preparation of cyclopropane-monocarboxylic acid by dry distillation of this dibasic acid, it was found that, by using a lower temperature than that called for by Perkin and by distilling the monobasic acid under diminished pressure as it formed, a better yield was secured.

When 36.4 g. of the dibasic acid was distilled slowly under diminished pressure and the distillate was fractionated, 11.6 g. of material was obtained. It boiled between 182° and 195°. On refractionation, nearly all of this substance distilled between 184° and 186°. This was practically pure cyclopropane-monocarboxylic acid. A small amount of this compound can be recovered by redistillation of the lower as well as the higher boiling fractions.

Attempts to prepare the ethyl ester by saturation of an alcoholic solution of this acid with dry hydrogen chloride gave a product which contained chlorine. This substance was ethyl chlorobutyrate produced by the splitting of the trimethylene ring.<sup>15</sup> In order to obtain the ester of cyclopropane-monocarboxylic acid, the method of Per-

<sup>13</sup> Perkin, *J. Chem. Soc.*, 47, 807 (1885).

<sup>14</sup> Ref. 11, p. 925.

<sup>15</sup> Boone and Perkin, *J. Chem. Soc.*, 67, 118 (1895); *Ber.*, 35, 2104 (1902). Kijner *J. Russ. Chem. Soc.*, 41, 659 (1909). Tanatar, *Z. physik. Chem.*, 41, 735 (1902). Kotz, *J. prakt. Chem.*, [11] 68, 153 (1903). Barthe, *Bull. soc. chim.*, [111] 35, 40 (1906).

kin<sup>13</sup> was followed. This required the silver salt. Since the silver salt is extremely soluble in water which contains small amounts of acid, of ammonia, or even of ammonium salts, a method for the preparation of the pure, solid ammonium salt was devised, so that a concentrated solution of it could be used to prepare the silver salt.

**AMMONIUM SALT.**—A stream of dry ammonia gas was passed through a solution of the free acid in anhydrous ether, kept cold throughout the operation by means of an ice-salt bath. After a short time, the ammonium salt began to separate as a voluminous white solid. It was collected and dried in a desiccator containing calcium oxide mixed with ammonium chloride. The dry salt melted at 115°. For analysis the ammonium salt was digested with aqueous sodium hydroxide and the ammonia was distilled into 0.1 *N* acid. The excess of acid was titrated with a solution of a standard base.


**Analysis.** Subs., 0.2149: 2.12 cc. of 1 *N* acid. Calc. for C<sub>4</sub>H<sub>7</sub>O<sub>2</sub>N: N, 13.87. Found: 13.82.

The salt was extremely soluble in water and in alcohol containing very small amounts of water. It could be kept for several months in a desiccator containing a mixture of calcium oxide and ammonium chloride.

**SILVER SALT.**—To 25 g. of the ammonium salt dissolved in a very small amount of water, the calculated amount of a concentrated solution of silver nitrate was added slowly, while the solution was stirred vigorously. The silver salt was collected and washed with cold water. Since this salt retained moisture very tenaciously, it was dried for some time at 110°, and then analyzed. The analysis confirmed the formula C<sub>4</sub>H<sub>5</sub>O<sub>2</sub>Ag, found by Perkin.

The dry salt was heated slowly in a test-tube immersed in a bath of sulfuric acid. At about 120°, it assumed a pale yellow color and, finally, a deep brown shade when the bath had reached 170°.

The Preparation of Ethyl Cyclopropane-monocarboxylate was carried out by refluxing a suspension of the silver salt in ether with ethyl iodide according to the method described by Perkin.

A. Cyclopropane-carboxyl-hydroxamic acid,  CHC(O)NHOH.—A solution

of 0.96 g. of sodium in methanol was added to a solution of 2.9 g. of hydroxylammonium chloride in 25 cc. of methanol. After this mixture had been cooled and filtered to remove sodium chloride, 4.2 g. of ethyl cyclopropane-monocarboxylate was poured into it. Finally, 0.84 g. of sodium in methanol was introduced and the mixture was allowed to stand over night in a warm place. After half an hour, a drop of the solution gave a deep purple color when acidified and treated with ferric chloride. The next morning dry carbon dioxide was passed into the solution thoroughly cooled, and the sodium carbonate which formed was removed by filtration. After evaporation of the alcohol, a viscous semi-solid mass resulted.

This mass was dissolved in water and treated with a solution of copper acetate. A grass-green copper salt of the hydroxamic acid was precipitated; it was collected, washed thoroughly with water and dried over sulfuric acid. When the dry copper salt had been pulverized carefully, it was suspended in methanol and a stream of dry hydrogen sulfide was passed through the suspension. The solution was filtered from copper sulfide and the methanol evaporated.

The product was a yellowish crystalline material possessing an odor characteristic of impure hydroxamic acids prepared from their copper salts by this method. Upon recrystallization of it from warm ethyl acetate, pure cyclopropane-monocarboxylic hydroxamic acid was obtained; it melted at 124° with decomposition. When ligroin is

added to the ethyl acetate solution, some of the yellow impurity is precipitated together with a part of the hydroxamic acid.

*Analyses.* Subs., 0.2145: 26.03 cc. of N (22.3°, 754. mm.). Calc. for  $C_4H_7O_2N$ : N, 13.86. Found: 13.92.

Subs., 0.21:  $H_2O$ , 0.1345;  $CO_2$ , 0.364. Calc. for  $C_4H_7O_2N$ : C, 47.5; H, 6.99. Found: C, 47.27; H, 7.16.

The hydroxamic acid was soluble in water, in methanol, in ethyl alcohol, and in hot ethyl acetate. It was only slightly soluble in ether and was insoluble in ligroin.

**B. Benzoyl Ester of Cyclopropane-Carboxyl-hydroxamic Acid,  $C_2H_5C(O)NHO-COC_2H_5$ .**—When an aqueous solution of the sodium salt of (A) was shaken with benzoyl chloride, the benzoyl ester mixed with benzoyl chloride and benzoic acid separated as a white mass. The product was collected and pressed on a porous plate and, when dry, was extracted repeatedly with boiling ligroin and recrystallized from hot ethyl alcohol to which water was added until a slight turbidity occurred. As the solution cooled, pure benzoyl ester separated in the form of white needles which were collected, washed with dilute alcohol and dried. It melted at 150°.

*Analyses.* Subs., 0.4931; 30.4 cc. of N (24.7°, 741 mm.). Calc. for  $C_{11}H_{11}O_4N$ : N, 6.83. Found: 6.9.

Subs., 0.1543:  $H_2O$ , 0.0772;  $CO_2$ , 0.3643. Calc. for  $C_{11}H_{11}O_4N$ : C, 64.36; H, 5.41. Found: C, 64.38; H, 5.59.

It is soluble in ether and in ethyl alcohol, but only slightly soluble in ligroin and is insoluble in water.

**POTASSIUM SALT OF (B).**—A solution of 0.4 g. of the benzoyl ester in absolute alcohol was cooled by means of an ice-salt bath, and treated with the calculated amount of potassium ethylate. The potassium salt, a white solid, was collected, washed with anhydrous ether and dried *in vacuo* over sulfuric acid. Anhydrous ether added to the filtrate precipitated more of the potassium salt. The dry salt puffed when it was heated to 103°. An isocyanate odor was detected and potassium benzoate was formed.

*Analysis.* Subs., 0.172:  $K_2SO_4$ , 0.0599. Calc. for  $C_{11}H_{11}O_4NK$ : K, 16.07. Found: 15.64.

A clear aqueous solution of 1.2 g. of the potassium salt, when heated to 90°, gave a white solid product. This was collected and washed with water. A portion of the filtrate was made slightly acid and, upon the addition of a solution of ferric chloride, an intense purple coloration was produced, which showed that a part of the benzoyl ester, formed by hydrolysis of the salt, had been hydrolyzed still further to yield some monohydroxamic acid. When the filtrate was acidified, carbon dioxide was evolved and 0.3 g. of benzoic acid was precipitated.

The solid product was extracted with a solution of sodium hydroxide, and from this solution 0.1 g. of the benzoyl ester was recovered. That portion of the solid which was insoluble in alkalis resembled the expected symmetrical di-cyclopropyl urea. It was insoluble in water, but very soluble in alcohol and in ether. However, the quantity obtained was too small to permit of complete purification and analysis. The partially purified solid melted between 172° and 178°.

When the dry potassium salt was heated until decomposition ensued, it gave a low-boiling oil, evidently cyclopropyl isocyanate. This oil was distilled and the vapor was passed into a small amount of aniline. The excess of aniline was removed by extraction with acid and the solid residue was crystallized from hot ether and ligroin. It melted at 151°, and its properties corresponded with those of phenyl-cyclopropyl urea,  $C_6H_5NHCONH(C_2H_5)$ , described by Kijner.<sup>14</sup>

<sup>14</sup> Kijner, *J. Russ. Chem.*, 47, 304-317 (1905).

**SODIUM SALT OF (B).**—A solution of 0.5 g. of the benzoyl ester in cold absolute alcohol was treated with the calculated amount of sodium ethylate. The addition of more than 6 volumes of anhydrous ether was required to precipitate the sodium salt. This was collected and dried *in vacuo* over sulfuric acid. The dry salt puffed at  $143^{\circ}$ ; a deposit of sodium benzoate remained in the test-tube and an isocyanate odor was noticed. An aqueous solution of the sodium salt behaved in a manner similar to that of the potassium salt described above.

**SILVER SALT OF (B).**—A solution of silver nitrate was added to a clear aqueous solution of the potassium salt. The white silver salt was collected, washed with water, then with alcohol, and finally with ether.

*Analysis.* Subs., 0.2468: Ag, 0.0843. Calc. for  $C_{11}H_{10}O_2NaAg$ : Ag, 34.57. Found: 34.16.

When the dry salt was heated above  $200^{\circ}$ , it decomposed and gave a strong isocyanate odor.

**C. Acetyl Ester of Cyclopropane-monocarboxyl-hydroxamic acid,  $(C_3H_5)CONHO-COCH_3$ .**—A slight excess of acetic anhydride was added to 1 g. of cyclopropane-monocarboxyl-hydroxamic acid. When the mixture was warmed gently, it became a clear liquid which solidified almost immediately. As the temperature was raised slightly, the product became liquid once more. This solution was stirred until a test portion failed to give a purple coloration with ferric chloride. The excess of acetic anhydride and of acetic acid was removed by placing the product in a vacuum desiccator over solid potassium hydroxide.

The ester, recrystallized from warm ether, formed very fine white needles so closely matted together that the product retained the shape of the filter paper upon which it was collected. Dried *in vacuo* over sulfuric acid, it melted at  $108^{\circ}$ .

*Analysis.* Subs., 0.2783: 24.2 cc. of N ( $23^{\circ}$ , 748 mm.). Calc. for  $C_6H_8O_2N$ : N, 9.78. Found: 9.87.

It was soluble in water, in alcohol, in acetone, in ethyl acetate, and in hot ether, but only slightly soluble in cold ether, and insoluble in ligroin.

**POTASSIUM SALT OF (C).**—A cold solution of 0.5 g. of the acetyl ester in absolute alcohol was treated with the calculated amount of potassium ethylate; upon the addition of anhydrous ether, the potassium salt was obtained as a white precipitate. This was separated, washed with ether, and dried *in vacuo* over sulfuric acid. The dry salt puffed when immersed in a bath previously heated to  $155^{\circ}$ .

*Analysis.* Subs., 0.0891:  $K_2SO_4$ , 0.0423. Calc. for  $C_6H_8O_2NK$ : K, 21.58. Found: 21.32.

## 2. Hydroxamic Acids Related to Dibenzylacetic Acid.

**The Preparation of Dibenzylacetyl Chloride,  $(C_6H_5CH_2)_2CHCOCl$ .**—Ethyl dibenzyl-aceto-acetate was prepared according to the method of Merz and Weith<sup>17</sup> and also that of F. Sesermann.<sup>18</sup> Both methods gave good results. This compound was made to undergo the "acid splitting," as described by Deikmann and Kron,<sup>19</sup> *vis.*, by refluxing it with sodium ethylate. The ethyl dibenzylacetate, thus produced, was saponified with alcoholic potash. One crystallization of the product from hot ligroin gave dibenzylacetic acid which melted at  $89^{\circ}$ . Its properties corresponded with the known properties of dibenzylacetic acid.

When 10 g. of dibenzylacetic acid was treated with an excess of thionyl chloride

<sup>17</sup> Merz and Weith, *Ber.*, 10, 759 (1877).

<sup>18</sup> Sesermann, *ibid.*, 6, 1086 (1873).

<sup>19</sup> Deikmann and Kron, *ibid.*, 41, 1266 (1908).

and the mixture was warmed, sulfur dioxide and hydrogen chloride were evolved and the reaction mixture became liquid. After this material had been refluxed for a short time the excess of thionyl chloride was distilled and the residual oil was submitted to fractional distillation under diminished pressure. When the last traces of thionyl chloride had been removed, the thermometer rose rapidly to 203°, and the entire product distilled between 203° and 205° under 17 mm. It was a yellow oil soluble in benzene and insoluble in water. It was hydrolyzed slowly in moist air.

**D. Dibenzylacet-hydroxamic Acid,  $(C_6H_5CH_2)_2CHCONHOH$ .** METHOD I.—A methanol solution containing 5.25 g. of hydroxylammonium chloride was treated with 1.7 g. of sodium in methanol. Sodium chloride was removed and the filtrate was treated with 20 g. of ethyl dibenzylacetate. These materials were thoroughly mixed and a solution of 1.5 g. of sodium in methanol was poured in. After several hours at room temperature, the mixture gave no test with ferric chloride for a hydroxamic acid. At the end of 18 hours, only a slight coloration was produced when ferric chloride was added to an acidified test portion of the reaction mixture. So the solution was warm several hours to 60° or 70° and the methanol allowed to evaporate.

This gave a white solid which was dissolved in a cold solution of sodium hydroxide and extracted with ether to remove any unchanged ester. When the solution was acidified, a solid white substance separated. This was collected, washed with water and pressed on a porous plate. The dry solid was extracted repeatedly with hot ligroin to remove any dibenzylacetic acid, and the undissolved dibenzylacet-hydroxamic acid was recrystallized from hot benzene. It melted at 146°. The yield was very small.

*Analysis.* Subs., 0.2718: 13.16 cc. of N (18°, 745.3 mm.). Calc. for  $C_{16}H_{17}O_2N$ : N, 5.49. Found: 5.57.

It was soluble in hot benzene, in alcohol, in alkalis and in ethyl acetate, but only slightly soluble in cold benzene and in ether, and insoluble in water or in ligroin. An alcoholic solution, made faintly acid with acetic acid, gave a grass-green copper salt when an alcoholic solution of copper acetate was added. An alcoholic solution of the hydroxamic acid reduced a solution of silver nitrate slowly.

**METHOD II.**—The following method gave dibenzylacet-hydroxamic acid practically quantitatively. To a solution of 10 g. of dibenzylacetyl chloride in dry benzene, slightly more than the calculated amount of free hydroxylamine was added. When the mixture was agitated, it became warm rapidly, so that it was necessary to cool the flask with tap water. Hydroxylammonium chloride and some of the hydroxamic acid separated as a white precipitate, while the excess of free hydroxylamine formed a gum which adhered to the side of the containing vessel. When the solution was heated to boiling, filtered while hot, and then cooled, pure dibenzylacet-hydroxamic acid separated. Its properties corresponded in every way with those described above.

**E. Benzoyl Ester of Dibenzylacet-hydroxamic Acid,  $(C_6H_5CH_2)_2CHCONHOCOC_6H_5$ .**—When an aqueous solution of 10 g. of dibenzylacet-hydroxamic acid with the calculated amount of alkali was cooled and shaken with benzoyl chloride, this ester separated as a white solid. This material collected and pressed on a porous plate. The dry product, extracted with hot ligroin several times to remove unused benzoyl chloride and benzoic acid, was crystallized from hot alcohol by addition of hot water until the solution became faintly turbid. As this mixture cooled, pure benzoyl ester of dibenzylacet-hydroxamic acid separated in the form of white needles which were collected, washed with cold, very dilute alcohol and dried. It melted at 147°.

*Analysis.* Subs., 0.3068: 10.2 cc. of N (20°, 746 mm.). Calc. for  $C_{22}H_{21}O_2N$ : N, 3.90. Found: 3.80.

The ester was soluble in alcohol; it was only slightly soluble in ether and was insoluble in water.

**POTASSIUM SALT OF (E).**—Five-tenths g. of the benzoyl ester was dissolved in cold absolute alcohol and treated with the calculated amount of potassium ethylate, upon the addition of over 10 volumes of anhydrous ether, only a very small amount of the solid salt was precipitated. This was collected and dried *in vacuo* over sulfuric acid. When the salt was heated on a spatula, it decomposed to give a vapor with an isocyanate odor, and potassium benzoate. When the salt was treated with cold water, an insoluble part always remained. This was washed with alkali and water. After it was crystallized from dil. alcohol, its properties corresponded with those of the synthesized *sym*.bi-dibenzylmethyl urea described below. When the potassium salt was dissolved in water at room temperature, a turbidity appeared immediately, and the corresponding disubstituted urea began to separate at once. Application of heat increased the speed of this reaction.

An attempt was made to prepare the sodium salt of (E) by the method used above in the preparation of the potassium salt. No precipitate was produced, even when several hundred cubic centimeters of anhydrous ether was added. An aqueous extraction of this alcohol-ether solution of the sodium salt soon gave the urea.

**SILVER SALT OF (E).**—A solution of 1 g. of the benzoyl ester in absolute alcohol was cooled to  $-10^{\circ}$ , and treated with slightly less than the calculated amount of potassium ethylate. Then an alcoholic solution containing slightly less than the calculated amount of silver nitrate was added to this cold solution. Only a small amount of a very light, fluffy precipitate resulted. However, upon the addition of anhydrous ether, the silver salt was obtained in quantity. This was collected, washed with absolute alcohol and with water, then again with absolute alcohol and finally with anhydrous ether. This silver salt, dried *in vacuo* over sulfuric acid, puffed at  $143^{\circ}$ , to give an oil which distilled into the cooler portions of the tube, while silver benzoate was left as solid. Evidently, this oil was dibenzylmethyl isocyanate, for upon treating it with warm water the corresponding urea was produced.

**Analysis.** Subs., 0.1860: Ag, 0.0428. Calc. for  $C_{28}H_{30}O_2NAg$ : Ag, 23.14: Found: 23.01.

**F. Acetyl Ester of Dibenzylacet-hydroxamic Acid,  $(C_6H_5CH_2)_2CHCON(H)OC(=O)CH_3$ .**—Five-tenths g. of pure dibenzylacet-hydroxamic acid and a slight excess of acetic anhydride were heated on a water-bath until a test portion failed to give a violet coloration with ferric chloride. As the product became cool, it solidified. It was kept over soda-lime in a vacuum desiccator until all traces of acetic acid and acetic anhydride had disappeared, and then recrystallized from hot benzene. It melted at  $126^{\circ}$ .

**Analysis.** Subs., 0.4194: 18.4 cc. of N ( $19^{\circ}$ , 741 mm.). Calc. for  $C_{18}H_{19}O_2N$ : N, 4.71. Found: 5.00.

The ester was soluble in hot benzene, in alcohol, in ethyl acetate and in acetone. It was only slightly soluble in ether and was insoluble in water and in ligroin. When a hot, saturated solution of the ester in absolute alcohol was cooled slowly, large, clear, square plates were obtained.

An attempt to prepare the potassium salt by dissolving 1.2 g. of (F) in cold absolute alcohol and adding to it the calculated amount of potassium ethylate failed to give any precipitate, even when more than 200 cc. of anhydrous ether was introduced. Traces of moisture absorbed during manipulation evidently effected rearrangement of some of the salt, for on evaporation of a part of the alcohol-ether solution *in vacuo* over sulfuric acid some *sym*.bi-dibenzylmethyl urea was obtained. In the preparation of the sodium salt, difficulties similar to those described in the preparation of the potassium salt were encountered.

**SILVER SALT OF (F).**—Five-tenths g. of the acetyl ester was dissolved in ab-

solute alcohol. To this solution, cooled to  $-12^{\circ}$ , slightly less than the calculated amount of an alcoholic solution of silver nitrate was added. When the walls of the containing vessel were scratched with a stirring rod, a white silver salt was precipitated. This was collected, washed with absolute alcohol, then with water, again with absolute alcohol, and finally with anhydrous ether.

The dry salt, heated slowly, turned brown at  $125^{\circ}$ , and suddenly black at  $145^{\circ}$ . When it was heated on a spatula, an isocyanate odor was detected. On exposure to light it turned purple. It was insoluble in water, in alcohol and in ether, but was soluble in ammonium hydroxide. A suspension of the salt in cold water containing the calculated amount of potassium bromide was shaken thoroughly and filtered from the silver bromide formed. When this solution was warmed, it gave a precipitate of *sym.* bi-dibenzylmethyl urea.

In order to prepare a sample of this urea for comparison, dibenzyl ketone made by the dry distillation of the calcium salt of phenylacetic acid, as described by Apitzsch,<sup>20</sup> was converted into the oxime, from which dibenzylmethyl amine was prepared according to the method described by Noyes.<sup>21</sup> The urea was synthesized from this amine as follows.

**G. Sym.-bi-dibenzylmethyl Urea,  $((C_6H_5CH_2)_2CHNH)_2CO$ .**—Phosgene was passed into a dry ether solution of the amine. Bi-dibenzylmethyl urea and dibenzyl-carbamine hydrochloride were precipitated as a white solid which was collected and extracted several times with boiling water in order to dissolve the amine hydrochloride. The crude urea, left after extraction, was recrystallized from hot alcohol and hot water. The pure urea separated in the form of small white needles which melted at  $159^{\circ}$ .

*Analysis.* Subs., 0.1407: 7.26 cc. of N ( $18^{\circ}$ , 748 mm.). Calc. for  $C_{21}H_{23}ON_2$ : N, 6.25. Found: 6.25.

It was soluble in ethyl acetate, in acetone, in alcohol, and in benzene, but was insoluble in water, in ether and in ligroin. A melting point was taken of a mixture of the urea synthesized above and of that formed as a product of the rearrangement of the different salts of the esters of dibenzylacet-hydroxamic acid. This melting point of the mixture was  $159^{\circ}$ .

### 3. Experiments with Tribenzylmethyl Chloride.

Tribenzyl carbinol was made from ethyl phenylacetate by the Grignard reaction according to Klages and Heilmann.<sup>22</sup> A considerable quantity of dibenzyl was obtained as a by-product.

**H. Tribenzylmethyl Chloride,  $(C_6H_5CH_2)_3CCl$ .**—To 10 g. of the carbinol, 15 cc. of acetyl chloride was added and the mixture was refluxed for hours. A short time after the refluxing was commenced the undissolved carbinol passed into solution. When the solution was allowed to cool very slowly, rosetts of colorless needles of tribenzylmethyl chloride separated. These needles were collected and washed thoroughly with anhydrous ether to remove acetyl chloride, acetic acid, and any unchanged carbinol.

After the chloride had been dried over calcium chloride, it melted at about  $173^{\circ}$  with decomposition.

*Analysis.* Subs.,<sup>23</sup> 1601: 4.15 cc. of 0.12094 N  $NaSCN$ . Calc. for  $C_{21}H_{21}Cl$ : Cl, 11.06. Found: 11.16.

<sup>20</sup> Apitzsch, *Ber.*, 36, 1428 (1904).

<sup>21</sup> Noyes, *Am. Chem. J.*, 14, 226 (1892).

<sup>22</sup> Klages and Heilmann, *Ber.*, 37, 1456 (1904).

<sup>23</sup> An analysis of this chloride was made by heating a sample of it with 10 g. of  $Na_2O_2$  in a Parr sulfur bomb. The usual Volhard method was employed to determine the chlorine.



It was soluble in hot benzene and in hot acetone. It was only very slightly soluble in ligroin, in cold benzene and in cold acetone. It was insoluble in water, in alcohol, and in ether.

Because of the ease of decomposition, the preparation of the chloride through the action of phosphorus trichloride or pentachloride on the carbinol was unsuccessful. The chloride could be recrystallized from acetyl chloride, but recrystallization from anhydrous benzene always lowered the melting point. It was very slowly decomposed by boiling water or by a boiling 10% solution of potassium hydroxide.

When the chloride was heated slightly above its melting point until the evolution of hydrogen chloride ceased, an oil formed which would not solidify when it was cooled in an ice-salt bath. This oil was soluble in ether, and an anhydrous ether solution of it decolorized bromine fairly rapidly. This seemed to indicate that the oil contained a compound of an unsaturated olefin nature, most likely dibenzyl-cinnamene,  $C_6H_5CH = C(CH_2C_6H_5)_2$ . This product was not investigated further.

**Behavior of the Chloride toward Magnesium (Grignard Reaction).**—An anhydrous ether solution of tribenzylmethyl chloride mixed with magnesium was refluxed for 8 hours. No evidence of a reaction could be detected, even when iodine was added. Methyl iodide also failed to start the reaction.

Because of the insolubility of the chloride in ether, anhydrous benzene was employed as the reaction medium. Iodine, methyl iodide, and aniline were used as "primers," and the solution was refluxed for 3 days without effect. When this benzene solution was cooled, needles of the chloride separated. These crystals melted at about  $165^\circ$ , instead of  $173^\circ$ , the melting point of the pure chloride.

#### 4. Hydroxamic Acids Related to Isobutyric Acids.

**I. Isobutyr-hydroxamic Acid or Dimethylacet-hydroxamic Acid,**  $(CH_3)_2CHC(O)-NH.OH$ .—Isobutyr-hydroxamic acid was made by two methods.

**METHOD I.**—A solution of 4.9 g. of sodium in methanol was poured into a methanol solution of 7.85 g. of hydroxylammonium chloride and the mixture cooled to  $-12^\circ$ . The sodium chloride was removed and 11.5 g. of methyl isobutyrate was added to the filtrate. After these substances were thoroughly mixed, 4.8 g. of sodium in methanol was introduced and the solution allowed to stand at room temperature overnight. When a test portion of the reaction mixture, removed immediately after the last addition of sodium methylate, was acidified it gave a pronounced color with ferric chloride. After 12 hours, a stream of dry carbon dioxide was passed through the solution to precipitate sodium carbonate. The product, thoroughly cooled in an ice-salt bath, was filtered from the sodium carbonate and the methanol was evaporated.

The solid, which consisted of sodium chloride and of isobutyr-hydroxamic acid, was dissolved in water made faintly acid with acetic acid. Upon the addition of an aqueous solution of copper acetate, a grass-green copper salt of the hydroxamic acid was precipitated. This salt was collected, washed with water, then with alcohol and finally with ether. After it had been dried thoroughly and pulverized, it was suspended in methanol and a stream of dry hydrogen sulfide was passed through the mixture. When the copper sulfide had been removed by filtration, and the ether evaporated, isobutyr-hydroxamic acid was obtained. Crystallized from ethyl acetate and ligroin, or from benzene, it melted at  $116^\circ$ .

**Analysis.** Subs., 0.0857: 10.35 cc. of N ( $21^\circ$ , 743 mm.). Calc. for  $C_4H_9O_2N$ : N, 13.60. Found: 13.73.

It was soluble in ether, in alcohol, in water, in acetone, in hot ethyl acetate, and in hot benzene. It was insoluble in ligroin.

**METHOD II.**—Isobutyric acid was refluxed a short time with thionyl chloride and the excess of this reagent was distilled. Isobutyryl chloride was obtained by fractionat-

ing the resulting oil. An anhydrous benzene solution of the acid chloride, kept thoroughly cooled by immersion in an ice-bath, was agitated vigorously with a slight excess of free hydroxylamine. When the reaction was complete, the solution was heated and filtered while hot. As the filtrate cooled, *isobutyr*-hydroxamic acid separated. It was recrystallized from ethyl acetate and ligroin. For the preparation of this particular hydroxamic acid, Method I was found to be preferable.

**J. Benzoyl Ester of *Isobutyr*-hydroxamic Acid,  $(\text{CH}_3)_2\text{CHCONHOCOC}_6\text{H}_5$ .—**This ester was prepared in two ways.

**METHOD I.**—*Isobutyr*-hydroxamic acid was treated with benzoyl chloride according to the Schotten-Baumann method. The precipitate was removed and pressed on a porous plate. When this crude material was extracted several times with hot ligroin and crystallized from a mixture of hot alcohol and hot water, the benzoyl ester of *isobutyr*-hydroxamic acid separated in the form of white needles; m. p.  $148^\circ$ .

**METHOD II.**—*Isobutyr*-hydroxamic acid was warmed on a water-bath with a slight excess of benzoic anhydride, until a test portion of the reaction mixture failed to give a violet color when treated with a solution of ferric chloride. The product solidified when cold. This mass was broken up, extracted several times with hot ligroin, and recrystallized from a mixture of hot alcohol and hot water. It formed white needles which melted at  $148^\circ$ .

**Analysis.** Subs., 0.2301: 14.01 cc. of N ( $24.3^\circ$ , 744 mm.). Calc. for  $\text{C}_{11}\text{H}_{14}\text{O}_4\text{N}$ : N, 6.77. Found: 6.85.

The benzoyl ester was soluble in alcohol, in ethyl acetate, and in hot benzene. It was slightly soluble in ether, and was insoluble in water and in ligroin.

**POTASSIUM SALT OF (J).**—A solution of 0.5 g. of the benzoyl ester of *isobutyr*-hydroxamic acid in absolute alcohol was immersed in an ice-salt bath, and 0.094 g. of sodium dissolved in absolute alcohol was added. Anhydrous ether caused a white precipitate to form which was collected, washed with anhydrous ether and dried over sulfuric acid. When the dry salt was heated slowly to  $200^\circ$ , no decomposition occurred; but when a portion in a test-tube was quickly thrust into a bath at  $150^\circ$  it puffed; an isocyanate odor was noticed and a deposit of potassium benzoate remained in the tube.

The salt obtained above was thought to be impure, so it was prepared a second time. In the second preparation, slightly less than the calculated amount of potassium ethylate was used and the salt was washed more thoroughly with anhydrous ether. It was placed over sulfuric acid in a desiccator immediately and the desiccator evacuated. In about 20 minutes, the salt decomposed spontaneously with such violence as to scatter potassium benzoate throughout the desiccator. When the desiccator was opened, it was found to be filled with the vapor of the isocyanate.

An aqueous solution of the potassium salt was warmed to  $50^\circ$  for some time. The light, oily layer which separated possessed a strong isocyanate odor. This solution, allowed to stand for several hours at room temperature, finally deposited a mass of fine white needles. These were collected, washed with alkali to remove any unchanged ester and any traces of *isobutyr*-hydroxamic acid produced by hydrolysis. Its properties were like those of the symmetrical di-*isopropyl* urea described by Hofmann.<sup>24</sup>

**SODIUM SALT OF (J).**—To 0.5 g. of the benzoyl ester dissolved in absolute alcohol and cooled to  $-10^\circ$ , 0.055 g. of sodium dissolved in absolute alcohol was introduced. Upon the addition of anhydrous ether, the white sodium salt was precipitated. This was collected, washed with ether and dried over sulfuric acid. At  $75^\circ$  it puffed, gave an isocyanate odor and left sodium benzoate in the tube. An aqueous solution of the sodium salt behaved in a manner analogous to that of the potassium salt described above.

<sup>24</sup> Hofmann, *Ber.*, 15, 756 (1882).

**SILVER SALT OF (J).**—An aqueous solution of the potassium or sodium salt was treated with an aqueous solution of silver nitrate. The white silver salt was collected, washed with water, then with a little alcohol, and finally with ether. When the dry silver salt was heated slowly in a test-tube, it turned brown at  $180^{\circ}$ . When the bath has reached  $200^{\circ}$  the sample was removed and passed through a free flame, whereupon it puffed vigorously; an isocyanate odor was noticed and silver benzoate remained in the tube. The silver salt prepared from the potassium salt gave the following analytical results.

*Analysis.* Subs., 0.0460: Ag, 0.0158. Calc. for  $C_{11}H_{11}O_2NaAg$ : Ag, 34.35. Found: 34.35.

**K. Acetyl Ester of Isobutyr-hydroxamic Acid,  $(CH_3)_2CHCONHOCOCH_3$ .**—A mixture of 1 g. of the hydroxamic acid and 1 cc. of acetic anhydride was warmed on a water-bath until a test portion failed to give a ferric chloride reaction. As the mixture became cool, the product solidified. The mass was broken up and placed in a vacuum desiccator over sodium hydroxide, where it remained until all the acetic anhydride had been removed. After it was recrystallized from hot benzene and ligroin, it melted at  $87^{\circ}$ .

*Analysis.* Subs., 0.2004: 17.45 cc. of N ( $21^{\circ}$ , 748 mm.). Calc. for  $C_6H_{11}O_3N$ : N, 9.65. Found: 9.95.

The acetyl ester was soluble in water, in hot ether, in hot benzene and in alcohol, but was insoluble in ligroin.

**POTASSIUM SALT OF (K).**—Upon the addition of ether to a cold absolute alcoholic solution of the acetyl ester of isobutyr-hydroxamic acid to which the calculated amount of potassium ethylate had been added, a white precipitate of the potassium salt was obtained. This was filtered, washed with anhydrous ether and dried. The potassium salt was very deliquescent; it absorbed sufficient moisture from the air to effect its solution in a very short time. A sample of the dry salt which had stood over sulfuric acid for 30 minutes, puffed when heated to  $53^{\circ}$ , and gave an isocyanate odor. After it had remained in the desiccator for several hours, it decomposed spontaneously as it was being removed from the desiccator.

When an aqueous solution of silver nitrate was added to a cold aqueous solution of the potassium salt, the silver nitrate was reduced and a mirror was formed upon the walls of the container. This reduction was caused by isobutyr-hydroxamic acid formed by hydrolysis. The presence of the hydroxamic acid was verified by a test with ferric chloride and by the formation of its copper salt.

### Summary.

1. The preparation and properties of the following new hydroxamic acids, together with their benzoyl and acetyl esters, are described.—(1) cyclopropane-carboxyl-hydroxamic acid; (2) isobutyr-hydroxamic acid; (3) dibenzylacet-hydroxamic acid.

The sodium, potassium and silver salts of many of these esters were made, and the conditions under which these salts rearrange were determined and compared.

2. The conclusions arrived at in this paper are, that the radicals present in the acyl groups from which these hydroxamic acids were derived influence the ease with which their derivatives suffer the Beckmann rearrangement in the following order: dibenzylmethyl > isopropyl > benzylmethyl > cyclopropyl.

3. During the investigation, it became necessary to improve the methods employed in the preparation of cyclopropane-monocarboxylic acid and its ammonium salt, and also, to synthesize the following new compounds: bi-dibenzylmethyl urea and tribenzylmethyl chloride. The failure of tribenzylmethyl chloride to react with magnesium to form a Grignard compound is discussed.

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## A NEW QUANTITATIVE METHOD FOR THE DETERMINATION OF IRON IN THE BLOOD.

BY ANSON L. BROWN.

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A new method for the determination of small amounts of iron in the blood which has been worked out in this laboratory offers possibilities for use in pathological laboratories and clinical diagnosis.

**Principle.**—A known amount of blood after laking in water is treated with conc. hydrochloric acid and a very small amount of potassium chlorate. By this method the proteins are precipitated and the iron rendered soluble. After heating in boiling water, the material is filtered and filtrate made up to a known volume. An aliquot portion of the filtrate is then compared colorimetrically with a standard iron solution.

**Method.**—To 4 cc. of distilled water contained in a test-tube 0.5 cc. of blood sample is added. After laking, 1 cc. of conc. hydrochloric acid and a very small amount of potassium chlorate (about 0.01 g.) are added. The test-tube and contents are then placed in boiling water and heated for about 15 minutes, until the liquid becomes white or light yellow and the proteins are entirely precipitated and have become white. The material is then allowed to cool and the residue to settle. The latter is then filtered and washed with water until 15 cc. of filtrate is obtained. After thoroughly shaking, 1.5 cc. of the filtrate is placed in one side of the test-tube colorimeter. To the other side of the colorimeter 0.25 cc. of the standard iron solution is added. To both tubes is added enough 0.1 *N* potassium permanganate solution to oxidize all the iron completely and until a permanent pink color remains. Then 5 cc. of 5 *N* ammonium thiocyanate solution is added and the standard diluted to 25 cc. with distilled water. The sample is then diluted until the two colors match. Should a brown residue form after the addition of ammonium thiocyanate solution, several drops of a 10% solution of hydrochloric acid are added to dissolve the precipitate.

### Solutions.

(1) **Standard Iron Solution.**—This solution is made by dissolving 0.7 g. of crystallized ferrous ammonium sulfate in 50 cc. of distilled water and adding 20 cc. of dil. sulfuric acid. The solution is warmed slightly and potassium permanganate added until the iron is completely oxidized, after which it is diluted to 1 liter. One cc. of this solution is equal to 0.1 mg. of iron.

(2) **Potassium Permanganate.**—This solution does not have to be standardized exactly but should be made approximately 0.1 *N*. It is prepared by dissolving 0.316 g. of potassium permanganate in 1000 cc. of distilled water.

(3) **Ammonium Thiocyanate.**—This is made approximately 5 *N* by dissolving 380 g. of iron-free ammonium thiocyanate in 100 cc. of distilled water.

### Calculation.

0.25 cc. of standard iron solution as above prepared is equivalent to 0.000025 g. of iron which has been diluted to 25 cc. Thus, when 1.5 cc. of the filtrate is used and the colors matched upon dilution to 17.5 cc. we obtain the ratio  $25 : .000025 :: 17.5 : x$ . Therefore  $x$  equals 0.000175 g. of iron in 1.5 cc. of the filtrate and in 15 cc. we obtain 0.000175 times 10 or 0.00175 g. of iron which is contained in 0.5 cc. of blood; in 100 cc. we obtain 200 times the above figure or 0.35 g. of iron or 35 mg. per 100 cc. of blood.

When the iron solution is made as above described and the amount of blood and reagents are used as directed, the calculations given above are not necessary and the iron can be calculated directly from the reading of the diluted sample by multiplying the reading by 2. Thus above where the reading of the sample was 17.5 it would become 35 after multiplying by 2. The above method has been checked very carefully against a method by Louis Berman<sup>1</sup> and the results agree very closely, as will be seen from the following data.

Brown		Berman
	Fe per 100 cc. of blood	
Mg.		Mg.
30		28
39		35
32		30
36		37
37		36
—		—
35 Av.		33 Av.

The above work was done on several different rabbits and at different times.

This method has been further checked by weighing a known amount of ferrous ammonium sulfate and adding a large excess of several other salts together with egg albumin. By using the method described above practically the same amount of iron was obtained as was theoretically present.

In order to ascertain whether all the iron present in the blood is dissolved by the treatments of concd. hydrochloric acid and potassium chlorate several samples of blood were ashed in a platinum crucible, treated with hot hydrochloric acid, washed with water and made up to a definite volume.

<sup>1</sup> Berman, *J. Biol. Chem.*, 35, 231 (1918); *C. A.*, 12, 1977 (1918).

An aliquot portion was then taken for analysis by the method as given above and the results obtained were as follows.

Whole blood	Ash
Iron per 100 cc. of blood	
Mg.	Mg.
38.0	39.0
30.0	32.0
42.0	42.5

The iron content of rabbit's blood varies from 27 to 42 mg. per 100 cc., while dog's blood varies from 40 to 48 mg. per 100 cc. and human blood from 45 to 52 mg. per 100 cc.

### Summary.

The method may be summarized as follows: 0.5 cc. of blood after laking in 4 cc. of water is treated with conc. hydrochloric acid and a very small amount of potassium chlorate placed in boiling water until white or light yellow, cooled and filtered, and the residue washed with water until 15 cc. of filtrate is obtained; an aliquot portion is then compared colorimetrically with standard iron solution using potassium thiocyanate as the indicator.

The advantages are: (1) A small amount of blood sample needed; (2) the analysis is rapid, not over 20 minutes being required; (3) greater accuracy is insured because the contrast in colors is more marked; (4) since it is a colorimetric method the results are more accurate with minute amounts than by either gravimetric or volumetric analysis.

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### NOTES.

**The Preparation of Phenylacetylene.**—Phenylacetylene has been prepared by a number of methods, the two outstanding ones being those of Glaser<sup>1</sup> and Holleman,<sup>2</sup> in which phenylpropionic acid is used, and the method of Nef,<sup>3</sup> which employs  $\omega$ -bromostyrene. In Nef's experiments, the bromostyrene was heated with potassium hydroxide and a small quantity of absolute alcohol. The products obtained were phenylacetylene and phenylvinyl-ether,  $C_6H_5CH=CHOC_2H_5$ , the yield of phenylacetylene being 60% of that calculated. Owing to the considerable conversion of starting material into by-product by Nef's method, the writer tried the use of molten potassium hydroxide instead of alcoholic potash.

The potassium hydroxide (80 g.) was placed in a distilling flask provided

<sup>1</sup> Glaser, *Ann.*, 154, 151 (1870).

<sup>2</sup> Holleman, *Ber.*, 20, 3080 (1887); *Rec. trav. chim.*, 15, 157 (1896).

<sup>3</sup> Nef, *Ann.*, 306, 264 (1899).

with a dropping funnel and a condenser. The flask was heated by means of an oil-bath at 200–235° (chiefly at 200–215°). Since the boiling point of phenylacetylene is 142–143°, and that of bromostyrene is 218–220°, the temperature of the molten potassium hydroxide was high enough to cause the phenylacetylene formed to distil from the unchanged bromostyrene. The latter was allowed to enter at the rate of about a drop a second, and the phenylacetylene soon distilled. From 25 g. of bromostyrene, 12.5 g. of phenylacetylene was obtained together with a small amount of water. The water was separated in a separatory funnel, and the phenylacetylene was dried with solid potassium hydroxide. Thus, 11 g. of apparently pure product boiling at 142–144° was obtained. This is a yield of practically 80% of the purified material.

A crust of potassium bromide is formed, and has a tendency to cover the melted potassium hydroxide, but this can be broken by means of a stirrer or by shaking the materials. The preparation of phenylacetylene is thus made comparatively easy.

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**The Successive Stages of the Hydrolysis of Tri-acetin.**—Since the publication of my article under this title,<sup>1</sup> my attention has been called to the extensive investigations of Professor Julius Meyer<sup>2</sup> in this field. This investigator studied the rate of acid hydrolysis and of alkaline saponification at different temperatures. He computed the velocity constants  $k_1$ ,  $k_2$ ,  $k_3$  of the single stages of hydrolysis from his experimental results by means of equations which he developed, and compared them with each other. In this way, the assumption of Geitel and Abel that  $k_1 : k_2 : k_3 = 1 : 2 : 3$  was demonstrated to hold both for the acid as well as for the alkaline hydrolysis. The saponification of other symmetrical polyesters, for instance the acetic acid ester of glycol, the ethyl ester of malonic and other dibasic acids, was also found to be in accord with this simple relation.

My results and conclusions, obtained by a different method both of experimental and theoretical treatment, entirely confirm these of Meyer.

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TOKYO, JAPAN.

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<sup>1</sup> Yamasaki, *THIS JOURNAL*, **42**, 1455 (1920).

<sup>2</sup> Meyer, *Z. Elektrochem.*, **13**, 186, 485 (1907); *Z. physik. Chem.*, **66**, 87; **67**, 257 (1909).

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TWENTY-EIGHTH ANNUAL REPORT OF THE COMMITTEE  
ON ATOMIC WEIGHTS

DETERMINATIONS PUBLISHED DURING 1921

BY GREGORY PAUL BAXTER<sup>1</sup>

Received January 27, 1922

The International Committee on Atomic Weights recommends<sup>1</sup> the following changes in its table.

Aluminum.....	27.0	Thulium.....	169.9
Bismuth.....	209.0	Silicon.....	28.1

At the Second International Conference of Pure and Applied Chemistry<sup>2</sup> at Brussels, in June, 1921, it was decided that the old International Committee on Atomic Weights should be enlarged and renamed the Committee on Chemical Elements, and that in addition to atomic weights, it should cover the fields of isotopes and radioactive elements.

Brauner<sup>3</sup> recommends to the New International Commission on Chemical Elements that the term "atomic weights" be confined to the values obtained by chemical methods and that the term "atomic masses" be used for the values of the individual isotopes of any given element. He also suggests that the proposed subcommittee of the International Commission be called a "Subcommittee for Atomic Weights."

<sup>1</sup> THIS JOURNAL, 43, 1751 (1921).

<sup>2</sup> J. Ind. Eng. Chem., 13, 737 (1921).

<sup>3</sup> Brauner, Chem. News, 123, 230 (1921).



A new (fourth) edition of Clarke's Recalculation of the Atomic Weights has been published as a Memoir of the National Academy of Sciences.<sup>4</sup>

Oddo<sup>5</sup> advocates a return to the hydrogen basis for the atomic weight system on the ground that the ratio between oxygen and hydrogen is now known with sufficient accuracy. The suggestion is also made that revisions of the atomic weight table be less frequent.

Moles<sup>6</sup> discusses critically determinations published in 1918-19.

Determinations published during 1921, besides some published during 1920, but not included in the last report are given below.

**Boron.**—Baxter and Scott<sup>7</sup> in a brief note announce that the analysis of both boron trichloride and boron tribromide has yielded the value 10.83 for the atomic weight of boron. This result is apparently in better accord with the isotopic ratio estimated by Aston than the recent result of Smith and Van Haagen (10.90).

**Oxygen.**—Moles and Gonzalez<sup>8</sup> have redetermined the density of oxygen prepared in different ways.

Series	Number of globes	Source of oxygen	Density
2	3	KMnO <sub>4</sub>	1.42882
4	3	KClO <sub>3</sub>	1.42849
5	3	KMnO <sub>4</sub>	1.42910
6	2	HgO	1.42929
7	3	KClO <sub>3</sub>	1.42875
8	3	HgO	1.42905
10	3	Ag <sub>2</sub> O	1.42869
11	2	KMnO <sub>4</sub>	1.42913
13	3	KMnO <sub>4</sub>	1.42872
14	3	KMnO <sub>4</sub>	1.42888
15	2	KMnO <sub>4</sub>	1.42890
16	3	Ag <sub>2</sub> O	1.42891
17	3	Ag <sub>2</sub> O	1.42884
18	3	KMnO <sub>4</sub>	1.42855
19	3	Electrolysis	1.42885
20	3	Electrolysis	1.42908
Mean			1.42889
Source of oxygen	Number of determinations	Density	
KMnO <sub>4</sub>	19	1.42886	
KClO <sub>3</sub>	6	1.42862	
HgO	5	1.42915	
Ag <sub>2</sub> O	9	1.42891	
Electrolysis	6	1.42897	

<sup>4</sup> Vol. XVI. Third Memoir, "The Constants of Nature." Part V. A Recalculation of the Atomic Weights. By F. W. Clarke. 1920.

<sup>5</sup> Oddo, *Gazz. chim. ital.*, 51, 161 (1921).

<sup>6</sup> Moles, *J. chim. phys.*, 18, 414 (1920).

<sup>7</sup> Baxter and Scott, *Science*, N. S., 44, 524 (1921).

<sup>8</sup> Moles and Gonzalez, *Compt. rend.*, 173, 355 (1921).

This result is more than 0.01% lower than the value usually assumed and, if used, will raise in this proportion the molecular weights of gases referred to oxygen.

**Fluorine.**—Moles and Batuecas<sup>9</sup> have corrected and recalculated their results upon the density of methyl fluoride.<sup>10</sup> After new corrections for the force of gravity at Madrid, for the barometric scale, and for the contraction of the globes when exhausted have been applied, the following densities are computed from the determinations at different pressures: 1 atm., 1.54507  $\pm$  0.00046;  $\frac{2}{3}$  atm., 1.53576;  $\frac{1}{3}$  atm., 1.52642. From these results  $\frac{(pv)_0}{(pv)_1} = 1 + \lambda$  is computed by Guye's "secondary difference" and "algebraic" methods to be 1.01803. In a following paper<sup>11</sup> these methods are shown to be mathematically identical.

New determinations of the density of oxygen prepared from potassium permanganate are presented.

Globe I	Globe I'	Globe II	Globe III
1.42870	.....	1.42946	1.42886
1.42939	.....	1.42949	1.42857
.....	.....	1.42903	1.42843
1.42872	1.42851	.....	1.42777
1.42892	1.42858	.....	1.42907
<hr/>		<hr/>	
Av. 1.42893	1.42855	1.42933	1.42854
		General mean	1.42882

The molecular weight of methyl fluoride is calculated, with the use of this value for the density of oxygen and the value 1.00097 for  $1 + \lambda$ , to be 34.025 and the atomic weight of fluorine to be 19.002 (C = 12.00; 3H = 3.023).

If the density of oxygen is taken as 1.4290, fluorine becomes 18.999.

**Chlorine.**—Mlle. Irene Curie<sup>12</sup> has compared the chlorine in certain geologically ancient minerals with ordinary chlorine. The minerals examined were sodalite from Bancroft, Canada, chlorapatite from Bamle, Norway, and an alkali chloride, probably formed by the weathering of Archaean granite, found in Dar Ouara, Central Africa. In every case barium chloride was prepared and used to precipitate known weights of silver nitrate, a comparison experiment with the same weight of silver nitrate and ordinary chloride being carried out at the same time.

The chlorine from sodalite and apatite is like ordinary chlorine within 0.02 unit of atomic weight, a quantity less than the experimental error. The material from Dar Ouara yielded slightly more silver halide than it

<sup>9</sup> Moles and Batuecas, *J. chim. phys.*, 18, 353 (1920).

<sup>10</sup> *Ibid.*, 17, 537 (1919).

<sup>11</sup> Page 599.

<sup>12</sup> Curie, *Compt. rend.*, 172, 1025 (1921).

Wt. of AgNO <sub>3</sub> G.	Source	Wt. of AgCl G.
0.3200	sodalite	0.2690
0.3200	ordinary	0.2689
3.8000	sodalite	3.2056
3.8000	ordinary	3.2060
1.4500	apatite	1.22295
1.4500	ordinary	1.22275
4.50000	alkali chloride	3.7963
1.7001	alkali chloride	1.4343
1.7001	ordinary	1.4330

should, indicating an atomic weight as high as 35.60. Iodine and bromine were shown to be absent in appreciable quantities. Further, more exact experiments are promised.

**Nickel.**—Baxter and Parsons<sup>13</sup> have compared terrestrial and meteoric nickel by reduction of the oxide. The meteoric nickel was obtained from a meteorite found near Cumpas, Sonora, Mexico, in 1903. Iron from this meteorite has already been shown to be identical with terrestrial iron.<sup>14</sup> Both specimens of nickel were carefully freed from iron and cobalt, and the oxide was produced by ignition of the nitrate. Besides reduction of the oxide in hydrogen, occluded gases were determined in each sample of oxide. The following weights are corrected for gas content of the oxide and to the vacuum standard.

	Wt. of NiO G.	Wt. of Ni G.	Ratio Ni:O	At. wt. Ni
Terrestrial	6.10962	4.80103	3.66886	58.702
	6.41296	5.03963	3.66964	58.714
	6.91037	5.43008	3.66825	58.692
	4.60083	3.61530	3.66838	58.694
	5.57105	4.37793	3.66931	58.709
	5.59224	4.39444	3.66876	58.700
		Av.	3.66887	58.702
Meteoric	6.65669	5.23021	3.66650	58.664
	4.45619	3.50201	3.67018	58.723
	4.64808	3.65209	3.66680	58.669
		Av.	3.66783	58.685

The difference between the two series is within the experimental error.

**Zinc.**—Baxter and Hodges<sup>15</sup> determined the zinc in zinc chloride by electrolytic deposition in a mercury cathode. The problem of preparing anhydrous neutral zinc chloride was solved by heating zinc bromide in a current of dry chlorine. Since, when weighed quantities of zinc were electrolytically transported through an aqueous electrolyte into a weighed mercury cathode, a fairly constant excess in weight of the factors

<sup>13</sup> Baxter and Parsons, *THIS JOURNAL*, 43, 507 (1921).

<sup>14</sup> Baxter and Thorvaldson, *ibid.*, 33, 337 (1911). Baxter and Hoover, *ibid.*, 34, 1657 (1912).

<sup>15</sup> Baxter and Hodges, *ibid.*, 43, 1242 (1921).

over the products of 0.23 mg. was found, this weight is subtracted in each experiment from the weight of zinc found in zinc chloride. Weights are corrected to vacuum.  $Cl = 35.457$ .

Wt. of $ZnCl_2$ G.	Wt. of Zn G.	Ratio $Zn:Cl_2$	At. wt. Zn
5.86823	2.81536	0.92220	65.397
5.24761	2.51698	0.92176	65.365
6.34043	3.04120	0.92179	65.368
2.43157	1.16657	0.92219	65.396
4.73689	2.27161	0.92144	65.343
5.98605	2.87068	0.92147	65.345
5.94448	2.85136	0.92184	65.371
5.80579	2.78416	0.92141	65.341
5.87593	2.81862	0.92193	65.378
4.00115	1.91975	0.92234	65.407
3.51882	1.68795	0.92194	65.378
Av.		0.92185	65.372

When Expts. 5, 6, 8 and 10, which are considered less trustworthy, are rejected the result becomes 65.379. This analysis of zinc chloride thus confirms the result obtained by analysis of zinc bromide, upon which the value in current use, 65.38, depends.

**Germanium.**—Müller<sup>16</sup> purified germanium material by processes which included (1) distillation of the chloride from hydrochloric acid solution in a stream of chlorine, (2) fractional crystallization of the hydrated oxide from aqueous solution. The fluogermanate of potassium was then synthesized from the purified germanium oxide, potassium carbonate and hydrofluoric acid. After repeated crystallization, the fluogermanate was prepared for an experiment by being heated to constant weight at 400–450°. Conversion to potassium chloride took place in a platinum bulb in a current of hydrogen chloride at temperatures ultimately high enough to melt the product. Weights are corrected to vacuum.  $K = 39.10$ ,  $Cl = 35.46$ ,  $F = 19.00$ .

Wt. of $K_2GeF_6$ G.	Wt. of $KCl$ G.	At. wt. Ge
1.94831	1.09814	72.37
3.09380	1.74350	72.41
2.10784	1.18774	72.44
2.36113	1.33044	72.44
4.38070	2.46863	72.42
1.52575	0.85970	72.45
4.00100	2.25483	72.40
Mean		72.418

**Cadmium.**—Baxter and Wilson<sup>17</sup> determined the cadmium in anhydrous cadmium sulfate by electrolytic deposition in a weighed mercury

<sup>16</sup> Müller, *THIS JOURNAL*, 43, 1085 (1921).

<sup>17</sup> Baxter and Wilson, *ibid.*, 43, 1230 (1921).

cathode. Blank experiments in which weighed buttons of pure cadmium were electrolytically transported through an aqueous electrolyte showed an average gain of 0.18 mg. A negative correction of this magnitude is applied to the weight of cadmium obtained in each analysis of cadmium sulfate. The cadmium sulfate was heated to constant weight in a current of air and sulfur trioxide at 700°. Weights are corrected to vacuum.  $S = 32.060$ .

Wt. of $\text{CdSO}_4$ G.	Wt. of Cd G.	Ratio Cd: $\text{SO}_4$	At. wt. Cd
3.65533	1.97033	1.16934	112.324
4.59450	2.47718	1.16996	112.386
4.12057	2.22166	1.16997	112.387
5.34263	2.88076	1.17015	112.405
6.19309	3.33940	1.17020	112.410
6.55765	3.53574	1.17004	112.394
6.04137	3.25735	1.17002	112.392
7.52884	4.06010	1.17048	112.437
6.58281	3.54949	1.17016	112.406
6.70646	3.61650	1.17040	112.429
6.56059	3.53730	1.17002	112.392
	Av.	1.17007	112.397
Av. of last 7 analyses.....		1.17019	112.409

This evidence supports the higher of the two conflicting values for this constant.

**Antimony.**—Willard and McAlpine<sup>18</sup> synthesized antimony tribromide from carefully purified antimony and bromine in an atmosphere of nitrogen in an all-glass apparatus. The product was fractionally distilled under a low pressure of nitrogen and was collected in sealed glass bulbs. After being weighed in an exhausted weighing bottle, the bulbs were broken under tartaric acid solution. The glass was collected and weighed and the solutions were precipitated with weighed equivalent amounts of silver. After the silver equivalent had been found, the silver bromide was collected. Material analyzed in the preliminary series was prepared from Kahlbaum's antimony. In Series B and D, metal reduced from the oxide by hydrogen was employed. In Series C the metal was reduced by sodium cyanide. Weights are corrected to vacuum.  $\text{Br} = 79.916$ .

Preliminary Series			
Wt. of $\text{SbBr}_3$ G.	Wt. of Ag G.	Ratio $\text{SbBr}_3:3\text{Ag}$	At. wt. Sb
2.54052	2.27493	1.11675	121.675
3.86859	3.46507	1.11645	121.577
4.07278	3.64722	1.11668	121.651
3.80772	3.40997	1.11664	121.638
4.72332	4.23070	1.11644	121.574
	Av.	1.11663	121.623

<sup>18</sup> Willard and McAlpine, *THIS JOURNAL*, 43, 797 (1921).

## Final Series B

Wt. of SbBr <sub>3</sub> G.	Wt. of Ag G.	Ratio SbBr <sub>3</sub> :3Ag	At. Wt. Sb	Wt. of AgBr G.	Ratio SbBr <sub>3</sub> :3AgBr	At. wt. Sb
4.17410	3.73672	1.11705	121.771	6.50517	0.641659	121.774
4.97693	4.45524	1.11710	121.787	7.75589	0.641697	121.775
5.97344	5.34702	1.11715	121.803	9.30873	0.641703	121.759
5.65589	5.06310	1.11708	121.781	8.81443	0.641663	121.756
	Av.	1.11710	121.786	Av.	0.641680	121.766

## Final Series C

3.64686	3.26462	1.11709	121.784	5.68301	0.641713	121.784
3.64435	3.26258	1.11701	121.758	5.67970	0.641645	121.746
3.35749	3.00574	1.11703	121.765	5.23284	0.641619	121.731
2.92082	2.61469	1.11712	121.794	4.55149	0.641728	121.793
	Av.	1.11706	121.777	Av.	0.641679	121.764

## Final Series D

3.39050	3.03541	1.11699	121.752	5.28506	0.641525	121.678
4.32024	3.86739	1.11709	121.784	6.73334	0.641619	121.731
4.70518	4.21221	1.11703	121.765	7.33279	0.641663	121.756
	Av.	1.11704	121.767	Av.	0.641602	121.722

The average value, 121.77, is more than a per cent. higher than the value recommended by the International Committee on Atomic Weights.

**Lanthanum.**—Baxter, Tani and Chapin<sup>19</sup> fractionated two specimens of lanthanum ammonium nitrate until the least soluble fractions were apparently free from cerium. Lanthanum chloride was prepared through the oxide and after being dried was compared with silver and silver chloride. No systematic differences could be detected between the different fractions examined. Vacuum weights are given. Ag = 107.880, Cl = 35.457.

Fraction of LaCl <sub>3</sub>	Wt. of LaCl <sub>3</sub> G.	Wt. of Ag G.	Ratio LaCl <sub>3</sub> :3Ag	At. wt. La
C 27	3.45559	4.55950	0.757888	138.912
C 3 + 4	5.75303	7.59134	0.757841	138.897
C 3 + 4	8.18782	10.80361	0.757878	138.909
T 1	6.80122	8.97359	0.757915	138.921
T 1	6.73670	8.88829	0.757930	138.925
T 5	5.43254	7.16772	0.757917	138.921
		Av.	0.757895	138.914
		Wt. of AgCl	Ratio LaCl <sub>3</sub> :3AgCl	
C 27	3.67748	6.44558	0.570543	138.969
C 3 + 4	5.33464	9.35255	0.570394	138.905
C 3 + 4	5.75303	10.08611	0.570391	138.904
C 3 + 4	8.18782	14.35625	0.570331	138.878
T 1	6.80122	11.92332	0.570413	138.913
T 1	6.73670	11.80952	0.570447	138.927
T 5	5.43254	9.52463	0.570368	138.893
		Av.	0.570413	138.913

<sup>19</sup> Baxter, Tani and Chapin, *THIS JOURNAL*, 43, 1080 (1921); a later note corrects errors in the tables (*ibid.*, 44, 328 (1922)). These corrections have been made in the above tables.

This value is nearly 0.1 unit lower than the one in common use.

**Bismuth.**—Classen and Ney<sup>20</sup> prepared bismuth triphenyl by the action of purified bismuth bromide on phenyl magnesium bromide, and purified the product by crystallization from alcohol and by distillation. After being dried in a high vacuum over phosphorus pentoxide, weighed amounts were heated with oxalic acid and a small amount of alcohol, at gradually increasing temperatures up to 750°. Constant weight of the resulting bismuth oxide was secured. Vacuum weights are given in the following table. H = 1.008, C = 12.005.

Wt. of Bi(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> G.	Wt. of Bi <sub>2</sub> O <sub>3</sub> G.	Ratio	At. wt. Bi
		2Bi(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> : Bi <sub>2</sub> O <sub>3</sub>	
5.45873	2.89068	1.88954	208.941
6.80350	3.60267	1.88962	208.920
3.51096	1.85942	1.88936	208.987
4.56421	2.41757	1.88909	209.059
5.17839	2.74216	1.88960	208.925
3.41677	1.80968	1.88921	209.027
2.34627	1.24281	1.88904	209.072
4.49340	2.38032	1.88933	208.996
4.55905	2.41489	1.88905	209.069
3.64677	1.93129	1.88942	208.971
Av.		1.88933	208.997

The average result agrees very well with the following value found by Hönigschmid and Birckenbach, but the latter point out that if C = 12.001 and H = 1.0077 the above value becomes 208.91.

**Bismuth.**—Hönigschmid and Birckenbach<sup>21</sup> have published a more extended account of the analysis of bismuth chloride,<sup>22</sup> which was summarized in the last report, and have in addition analyzed bismuth bromide. Both salts were prepared by synthesis from several specimens of purified metal and the corresponding halogen, and after sublimation in a current of dry nitrogen were transferred to a weighing bottle without exposure to moisture. After the salt had been dissolved in 3 N nitric acid, to avoid hydrolysis, it was compared with silver and finally the silver halide was collected. Experiments with potassium halides showed that the nitric acid caused no loss of halogen. Series I was included in the last report, but since a small correction has been subsequently applied for silver contained in the distilled water, owing to the use of a silver condenser, and since a few additional experiments are included, the results of this series are given again. Weights are in a vacuum. Cl = 35.457, Br = 79.916, Ag = 107.880.

<sup>20</sup> Classen and Ney, *Ber.*, **53B**, 2267 (1920); *Z. anorg. allgem. Chem.*, **115**, 253 (1921).

<sup>21</sup> Hönigschmid and Birckenbach, *Ber.*, **54B**, 1873 (1921).

<sup>22</sup> Hönigschmid, *Z. Elektrochem.*, **26**, 403 (1920).

## SERIES I

Sample	Wt. of BiCl <sub>3</sub>	Wt. of Ag	Ratio		Wt. of AgCl	Ratio	
			BiCl <sub>3</sub> : 3Ag	At. wt. Bi		BiCl <sub>3</sub> : 3AgCl	At. wt. Bi
1	3.29894	3.38572	0.974369	208.97	4.49789	0.733442	209.02
1	3.54331	3.63644	0.974390	208.98	4.83067	0.733503	209.04
1	4.74125	4.86573	0.974417	208.99	6.46455	0.733423	209.01
1	2.64020	2.70984	0.974301	208.95	3.59956	0.733479	209.03
1	4.49476	4.61253	0.974467	209.01	6.12841	0.733430	209.01
1	5.19912	5.33556	0.974428	208.99	7.08896	0.733411	209.00
1	4.36220	.....	.....	.....	5.94742	0.733461	209.03
1	4.42249	.....	.....	.....	6.02960	0.733463	209.03
3	4.82566	.....	.....	.....	6.57976	0.733408	209.00
2	4.99471	5.12592	0.974402	208.99	6.80969	0.733471	209.03
2	5.29284	5.43179	0.974419	208.99	7.21652	0.733434	209.01
2	4.62983	4.75126	0.974442	209.00	6.31252	0.733436	209.02
2	5.67213	5.82103	0.974420	208.99	7.73383	0.733418	209.01
5	5.69460	5.84417	0.974407	208.99	7.76479	0.733388	208.99
5	5.96312	6.11973	0.974409	208.99	8.13087	0.733393	209.00
4	5.57877	.....	.....	.....	7.60652	0.733419	209.01
4b	6.24054	6.40429	0.974431	208.99	8.50911	0.733395	209.00
2	6.30709	6.47269	0.974416	208.99	8.60003	0.733380	208.99
6	5.88272	.....	.....	.....	8.02168	0.733352	208.98
6	4.46068	4.57809	0.974354	208.97	6.08213	0.733407	209.00
Weighted Mean			0.974406	208.99		0.733426	209.01

## SERIES II

Wt. of BiBr <sub>3</sub>	Wt. of Ag	Ratio		Wt. of AgBr	Ratio	
		BiBr <sub>3</sub> : 3Ag	At. wt. Bi		BiBr <sub>3</sub> : 3AgBr	At. wt. Bi
7.29339	.....	.....	.....	9.15727	0.796458	208.97
5.39630	.....	.....	.....	6.77528	0.796468	208.97
3.70766	.....	.....	.....	4.65512	0.796469	208.97
5.60993	4.04608	1.38651	208.98	7.04331	0.796490	208.99
4.31679	3.11345	1.38650	208.98	5.41993	0.796466	208.97
6.08198	4.38645	1.38654	208.99	7.63592	0.796496	208.99
5.79839	4.18189	1.38655	208.99	7.27982	0.796501	208.99
5.57802	4.02293	1.38656	209.00	.....	.....	.....
6.12608	4.41819	1.38656	209.00	.....	.....	.....
5.49745	.....	.....	.....	6.90203	0.796498	208.99
5.94212	4.28542	1.38659	209.01	7.46066	0.796460	208.97
5.36148	3.86663	1.38660	209.01	6.73168	0.796454	208.97
5.44985	3.93049	1.38656	209.00	.....	.....	.....
5.02784	3.62606	1.38658	209.01	6.31276	0.796457	208.97
5.05097	3.64271	1.38660	209.01	.....	.....	.....
3.91823	2.82605	1.38647	208.97	4.91968	0.796440	208.96
4.90320	.....	.....	.....	6.15616	0.796470	208.97
6.40360	4.61829	1.38657	209.00	8.03956	0.796511	209.00
Weighted Mean		1.38655	209.00		0.796474	208.98



## SERIES III

Wt. of BiCl <sub>3</sub>	Wt. of Ag	Ratio BiCl <sub>3</sub> : 3Ag	At. wt. Bi	Wt. of AgCl	Ratio BiCl <sub>3</sub> : 3AgCl	At. wt. Bi
5.92659	6.08198	0.974451	209.00	8.08075	0.733429	209.01
5.67415	5.82301	0.974436	209.00	7.73633	0.733442	209.02
5.67569	5.82448	0.974454	209.00	7.73886	0.733401	209.00
6.01087	6.16839	0.974467	209.00	8.19606	0.733385	208.99
3.99300	4.09773	0.974441	209.00	5.44469	0.733375	208.99
6.69026	6.86567	0.974451	209.00	9.12219	0.733405	209.00
6.06332	6.22248	0.974421	208.99	8.26735	0.733405	209.00
6.26505	6.42952	0.974419	208.99	8.54321	0.733337	208.97
4.82012	4.94648	0.974454	209.00	6.57250	0.733376	208.99
6.44339	6.61235	0.974448	209.00	.....	.....	.....
6.04882	6.20743	0.974448	209.00	8.24779	0.733387	208.99
1.77359	1.82015	0.974419	208.99	2.41846	0.733355	208.98
6.42838	.....	.....	.....	8.76453	0.733454	209.02
3.58931	.....	.....	.....	4.89385	0.733432	209.01
4.91588	.....	.....	.....	6.70282	0.733404	209.00
5.70608	.....	.....	.....	7.78038	0.733393	209.00
Weighted Mean		0.974442	209.00	0.733399		209.00

## SERIES IV

Wt. of BiBr <sub>3</sub>	Wt. of Ag	Ratio BiBr <sub>3</sub> : 3Ag	At. wt. Bi	Wt. of AgBr	Ratio BiBr <sub>3</sub> : 3AgBr	At. wt. Bi
7.64984	5.51723	1.38654	208.99	.....	.....	.....
5.73427	4.13564	1.38655	209.00	.....	.....	.....
6.74400	4.86378	1.38658	209.00	8.46713	0.796491	208.99
5.69756	4.10915	1.38655	209.00	7.15302	0.796525	209.01
3.11177	2.24420	1.38655	208.99	3.90698	0.796464	208.97
5.91488	4.26588	1.38656	209.00	.....	.....	.....
7.07209	5.10050	1.38652	208.99	.....	.....	.....
3.91069	2.82047	1.38654	208.99	.....	.....	.....
4.59461	3.31368	1.38656	209.00	.....	.....	.....
7.07280	5.10087	1.38659	209.00	.....	.....	.....
5.35474	.....	.....	.....	6.72284	0.796500	208.99
Weighted Mean		1.38655	209.00	0.796495		208.99

The general mean of all the series is 209.00.

During recent years the application of positive ray analysis by Thompson, Aston and Dempster has furnished experimental evidence that many at any rate of the elements are mixtures of isotopes having atomic weights which are very nearly integers referred to oxygen as 16, the "chemical" atomic weight being the statistical average of the components in the mixture. A list of the isotopes of the existence of which there is experimental evidence is given below.<sup>22</sup> Radioactive disintegration products are omitted.

<sup>22</sup> Aston, *Phil. Mag.*, **42**, 143 (1921); **42**, 440 (1921); *Nature*, **107**, 520 (1921).  
Dempster, *Science N. S.*, **52**, 559 (1920); *Phys. Rev.*, **17**, 427 (1921).

Element	Atomic number	Atomic weight	Minimum number of isotopes	Mass of isotopes in the order of intensity
H	1	1.008	1	1.008
He	2	3.99	1	4
Li	3	6.94	2	7, 6
B	5	10.9	2	10, 11
C	6	12.00	1	12
N	7	14.01	1	14
O	8	16.00	1	16
F	9	19.00	1	19
Ne	10	20.2	2	20, 22 (21)
Na	11	23.00	1	23
Mg	12	24.36	3	24, 25, 26
Si	14	28.1	2	28, 29 (30)
P	15	31.04	1	31
S	16	32.06	1	32
Cl	17	35.46	2	35, 37 (39)
A	18	39.88	2	40, 36
K	19	39.10	2	39, 41
Ni	28	58.68	2	58, 60
As	33	74.96	1	75
Br	35	79.92	2	79, 81
Kr	36	82.92	6	84, 86, 82, 83, 80, 78
Rb	37	85.45	2	85, 87
I	53	126.92	1	127
X	54	130.2	5 (7)	129, 132, 131, 134, 136, (128), (130?)
Cs	55	132.81	1	133
Hg	80	200.6	(6)	(197-200), 202, 204

It is to be noted, however, that radium-lead of atomic weight as low as 206.06 has been isolated,<sup>24</sup> and thorium-lead as high as 207.9.<sup>25</sup> The relation of these to ordinary lead remains to be determined. Thorium containing ionium has been found to have a lower average atomic weight than thorium.<sup>26</sup>

Experimental evidence of the partial separation of the isotopes of neon has been obtained by Aston and Lindemann,<sup>27</sup> of chlorine by Harkins<sup>28</sup> and by Brönsted and von Hevesy,<sup>29</sup> and of mercury by Brönsted and von Hevesy<sup>30</sup> and by Harkins.<sup>31</sup>

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<sup>24</sup> Hönlgschmid and Mme. St. Horovitz, *Sitzb. k. Akad. Wien., Abt. IIA*, 123, 1 (1914); *Monatsh.*, 36, 355 (1915). Richards and Wadsworth, *THIS JOURNAL*, 38, 2613 (1916).

<sup>25</sup> *Z. Elektrochem.*, 25, 91 (1919).

<sup>26</sup> Hönlgschmid, *ibid.*, 22, 18 (1916).

<sup>27</sup> Aston, *Report Brit. Ass. Adv. Sci.*, 1913, 403. Aston and Lindemann, *Phil. Mag.*, 39, 450 (1920).

<sup>28</sup> Harkins, *Phys. Rev.*, 15, 74 (1920); *Science, N. S.*, 51, 289 (1920); *Nature*, 105, 230 (1920). Harkins and Hayes, *THIS JOURNAL*, 43, 1803 (1921).

<sup>29</sup> Brönsted and von Hevesy, *Nature*, July, 1921.

<sup>30</sup> Brönsted and von Hevesy, *ibid.*, Sept., 1920; *Z. physik. Chem.*, 99, 189 (1921); *Phil. Mag.*, 43, 31 (1922).

<sup>31</sup> Harkins, *THIS JOURNAL*, 44, 37 (1922).

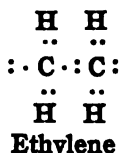
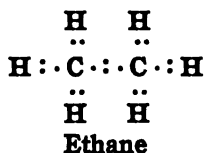
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]  
**DOUBLE AND TRIPLE BONDS, AND ELECTRON STRUCTURES  
 IN UNSATURATED MOLECULES**

By E. D. EASTMAN

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The conception of multiple bonds which will be presented here is based upon the Lewis<sup>1</sup> theory of molecular structure and valence, but departs from it in several essential respects. Among the more important differences is the assumption that while the group of eight<sup>2</sup> is usually maintained about each atomic kernel in any molecule, the valence bonds, whether "single" or "multiple," consist almost universally of but two electrons, mutually shared by two atoms.<sup>3</sup>

To show how this state might be realized, it will be recalled that the elements comprising the first period, lithium to fluorine, each possess 2 electrons which ordinarily do not act as valence electrons.<sup>4</sup> They appear to form a sort of primary "shell," persisting through the entire period of elements and appearing also in hydride ion and in helium. In helium the group of two is very stable but in hydride ion it is much less so. In the other elements it may be intermediate between these two extremes, and it is possible that under circumstances which make it difficult for the group of eight to be completed about them, the inner electrons may themselves take part in the formation of octets. Adopting this hypothesis, the picture of the double bond which is now proposed is that of one atom in which the central electrons have been drawn into the outer octet, joined by two electrons to another atom in which the normal arrangement is preserved. In cases of triple bonding the inner two electrons are assumed to have been drawn into the outer shell in each of two adjacent atoms, there being again two electrons held in common. These linkings are illustrated and compared with the saturated bond in the accompanying formulas of ethane, ethylene and acetylene. The symbols here represent atomic nuclei, and all electrons outside are indicated by dots.



<sup>1</sup> Lewis, THIS JOURNAL, 38, 762 (1916). Langmuir, *ibid.*, 41, 868 (1919).

<sup>2</sup> Langmuir, *ibid.*, 42, 274 (1920) emphasizes the importance of the octet of electrons.

<sup>3</sup> The two electron double bond is also assumed in the "sextet" theory of Rodebush and Latimer, *ibid.*, 42, 1419 (1920).

<sup>4</sup> For example, taking the atomic number of carbon, 6, to represent the positive charge of the nucleus, there must be 6 electrons outside of the nucleus. Of these, 4 are the so-called valence electrons, leaving 2 which do not act as bonds in saturated compounds.

In the succeeding sections of this article the more general aspects of the above ideas will first be developed, following which specific applications will be made to the properties and reactions of various unsaturated substances.

### General Considerations

**Specification of Elements which can Form Multiple Bonds.**—From a study of the properties of numerous substances, Lewis concludes that the ability to form non-polar multiple bonds is peculiar to the first period elements.<sup>5</sup> The same conclusion follows readily from the present theory. Once a complete shell is formed about the inner two electrons the possibility of their participation in bond formation should be almost or quite excluded. This would lead to the requirement that one at least of any two doubly bonded atoms, and both atoms of a triple bond, must be of the first period.

Differentiation among the elements within the period, so far as bonding is concerned, is perhaps to be traced to the differing nuclear charges. Lithium, with its small charge, should more readily lose 1 electron, reverting to the group of 2, than gain 5, forming an unsaturated octet. The fluorine nucleus because of its large charge should easily gain and hold the one electron needed to complete both shells about it. The middle elements only will then show tendencies to form the unsaturated group.

**Laws of Force.**—The laws of force which hold at short distances between positively charged particles, between negative electrons, and between positive and negative particles, are of great importance in any theory of atomic or molecular structure. Unfortunately very little is known concerning these laws. From experiments<sup>6</sup> on scattering of  $\alpha$  particles it is indicated that the inverse-square law of repulsion of positive particles holds to within  $10^{-11}$  cm. of the nuclei of certain metallic atoms. The inverse-square law of repulsion is usually assumed to hold for electrons also. The paired electrons of the Lewis tetrahedral atom, however, require the assumption that electrons in the shells of atoms attract each other when close together. The little independent evidence which exists on this point is negative in character. Fewer double charges are obtained,<sup>7</sup> for example, when the molecules of air or particles of shellac or sulfur are ionized by various agents than might be expected if the electrons which are expelled exist in closely associated pairs. In spite of this, the attractive

<sup>5</sup> The author's thanks are due to Professor Lewis for permission to include this generalization, which has not been published. Its significance hinges largely on the idea of the non-polar bond. Thus molecules containing only such bonds have small external fields, form low melting, readily volatile substances, etc., ideas which are elaborated in the several papers already referred to. Here it will only be said that there are few, if any, exceptions to the rule above.

<sup>6</sup> Chadwick, *Phil. Mag.*, 40, 734 (1920).

<sup>7</sup> Millikan and Fletcher, *ibid.*, 21, 753 (1911). Kelly, *Phys. Rev.*, 16, 260 (1920).

force idea presents many appealing features, and it may be necessary later to accept it. At the present time, however, it appears desirable to do without this assumption if possible.

Turning to the case of a positive and a negative particle, Lewis<sup>8</sup> points out that Coulomb's law must fail at short distances, and suggests that the force changes periodically in a certain region from attraction to repulsion. In Fig. 1<sup>9</sup> which depicts one such possibility, the force,  $f$ , between particles is plotted against the distance,  $r$ , separating them. The inverse-square law is not approached until  $r$  is relatively large. The points A, B and C represent equilibrium positions to which electrons displaced by small amounts would tend to return. That a number of such positions<sup>10</sup> are present in or about all atoms cannot be doubted. For purposes of illustration and with no intent to assign definite causes or laws, Fig. 1 will be

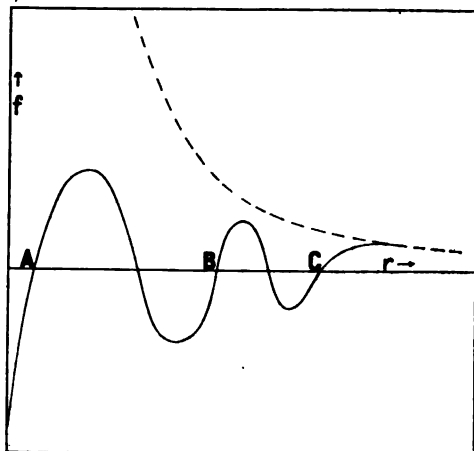


Fig. 1.—Deviations from Coulomb's Law.

assumed to represent this condition in a rough qualitative way, and will be used to correlate the facts discussed under the following topics.

**Formation of "Extended Octets."**—In saturated molecules, the inner 2 electrons of a carbon atom may be imagined to be located, for example, at A in Fig. 1, while the shell of 8 has the radius B. The formation of a multiple bond requires the exertion of powerful disruptive forces upon the electron shells (as in the splitting off of

chlorine atoms with their tightly held electrons). Under such influences, 2 of the 10 electrons are lost entirely by the atom, and the inner 2, together with the remaining 6 of the original octet, are assumed to be drawn out to form a new shell of larger size at C. The increased size assumed and the absence of the center electrons has suggested the designation of this group as the "extended octet."

**Reactivity and Stability.**—The new grouping is well suited to represent the characteristics of unsaturated bodies. These in general cannot be classed as highly reactive, which is attested by the fact that in the typical cases they are thermodynamically unstable. They should therefore decompose into other substances if they were reactive. The presence of the

<sup>8</sup> Lewis, *Science*, N. S., 46, 297 (1917).

<sup>9</sup> From a paper by Dushman, *Gen. Elec. Rev.*, 20, 407 (1917).

<sup>10</sup> Corresponding in the static atom to the different orbits of Bohr's model.

octet structure may account in part for this lack of great activity. The possibility of returning to the regular grouping, and the weakened constraints on the electrons (indicated by the smaller slope of the curve in Fig. 1 near the outer equilibrium positions) render them more reactive than similar saturated bodies.

The change with temperature in the stability of such a substance as acetylene is interesting. At ordinary temperatures the amplitudes of the electrons in Position C in Fig. 1 will be small. As the temperature is increased, however, they gain sufficient energy to carry them past the minimum in the curve to the left of C. Their transfer to the inner positions is then spontaneous, and a reaction occurs, the products of which are carbon (with the normal octet) and hydrogen. As the temperature is still further increased, the thermal energy of the electrons becomes so great that they can no longer remain in the inner positions, and the formation of the extended octet is favored. Acetylene therefore becomes stable with respect to hydrogen and carbon.

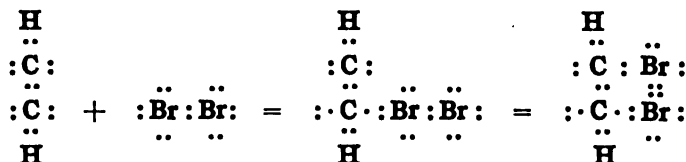
**Arrangement of Electrons.**—For the sake of simplicity the arrangement of electrons in all octets has been assumed to be essentially cubic. In all probability the actual structures are often intermediate between cubes and tetrahedra, and may closely approach the latter, on account of the attraction exerted by the nuclei on the electrons of the bonds. A grouping by twos (which is in no sense pairing due to attraction) may also result if there is a maximum in the repulsion-distance curve of electrons, as assumed by Mr. Huggins of this Laboratory. In any event the tetrahedral direction of the four bonds in saturated compounds is no doubt maintained. It is this direction of bonds, rather than any atomic configuration, which has been valuable in organic chemistry.

For the sake of convenience in representation, no attempt is made in general in the formulas of this paper to indicate distortions from the cubic arrangement or the enlarged size of extended octets.

**Free Rotation.**—The differences between single or triple bonds and the double bonds of this theory should not be overlooked. The structures about the former two are entirely symmetrical. In the latter this symmetry is absent. Due to the different sizes of the connected octets, the electrons in double bonds are probably spread apart farther than usual in the normal bond. The abnormal stresses which result between the electrons of the bond and those of each of the adjoining structures (perhaps even involving the inner electrons of the normal octet) might easily be such as to oppose free rotation of the atomic shells with respect to each other. Indeed, when analyzed in this light there is little difference between the 2-electron bond of this theory and the 4-electron bond with the tetrahedral arrangement. Especially when it is recalled to what extent

the prevention of rotation is due to specific effects,<sup>11</sup> it appears that differences of the double from the single bond are of degree only, and the ideas above provide sufficient basis for the interpretation of the facts.

**Type Reactions.**—The substances which may add directly to unsaturated bodies are confined to two fairly definite groups, the one consisting of bodies like the halogens and halogen hydrides, the other embracing substances which are themselves unsaturated. The molecules of the first type may be regarded as potentially ionized, or ready to separate with an unequal division of electrons between two atoms. When a bromine molecule, for example, collides with a molecule of acetylene the rearrangement indicated below may be assumed to occur. The reaction may be



described as the telescoping of one of the bromine<sup>12</sup> atoms with one of the extended octets, the breaking of the loose bond of bromine to bromine, and the attachment of the second bromine atom to the other carbon octet, sharing two of its electrons. By a repetition of this process another molecule of bromine might be added. The condensation of molecules in which there are multiple bonds is similar to the first stage above. As illustrated in the next section, it consists simply in the telescoping of two extended octets, the regular double bond arrangement being formed. The saturated carbon octet does not usually show this property of telescoping with one of the extended octets, probably because the former is always protected by surrounding atoms.

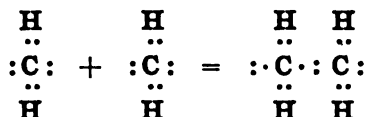
### Structures and Properties of Typical Substances

**Chain Hydrocarbons.**—The simplest hydrocarbon which should exist according to the present theory is methylene. It is, however, a high temperature form, and the failure of the numerous attempts to prepare it is evidence that it is too reactive to exist at ordinary temperatures. Its condensation to ethylene offers the simplest example of the second type of reaction of the preceding section and for this reason is shown below.

Ethylene and acetylene have already been used as type substances. It remains only to point out that when all of the electrons in the outer

<sup>11</sup> As evidenced by the differing temperatures at which different unstable forms go over to their stable isomers. In those syntheses where only a single form is produced, it even seems that the rate of transformation of the unstable to the stable form is high even at ordinary temperatures.

<sup>12</sup> Symbol letters for elements after the first period represent the entire atomic kernel.



shell are not acting directly as bonds, the attached hydrogen nuclei (positive electrons) no doubt have some freedom of motion from one position to another. This is illustrated in the formulas below, which are also used to introduce a method of representation which will prove convenient later.



Fig. 2.—Formulas of ethane, ethylene and acetylene.

By this plan the projections of the electron cubes are indicated by squares. Figs. 2 and 3 show ethane, ethylene and acetylene, with possible tautomeric forms of the last two. In some of these, certain of the hydrogen nuclei are assumed to be held jointly by 4 electrons.

A substituted ethylene could, by the present theory, exist in two isomeric forms. Thus propylene might have either of the two formulas of Fig. 4.

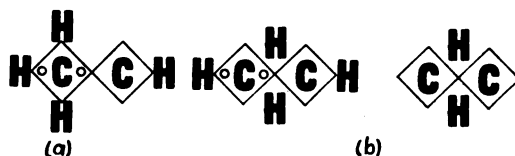


Fig. 3.—Modified formulas of ethylene and acetylene.

But the physical properties of such isomers could hardly differ sensibly, and no chemical method could distinguish between them. However, in a chain of 4 or more carbon atoms with one double bond, the "position" of the latter is not necessarily uniquely determined. The molecule represented in Fig. 5 might break on oxidation at either side of the extended carbon atom, and the second of the two added halogen atoms might in the

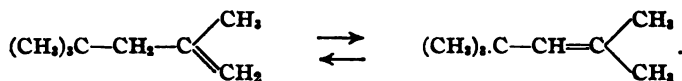


Fig. 4.—Formulas of propylene.

same way go to either of the adjacent normal octets. In general, due to the dissymmetry of the molecule, reactions will be "directed" so that they occur mainly in one way. Sometimes, however, these directive influences will be weak and the molecule will not react exclusively in either way. This behavior is experimentally found in the case of *iso*-dibutylene, and the



single formula of Fig. 5 takes the place of two of the ordinary ones, represented in tautomeric equilibrium below.



It is not desired to imply that actual shifting of a double bond between tautomeric or isomeric forms will never be found, for a mechanism involving little disturbance of the molecule as a whole is possible by the present theory. This may consist simply in the passage of the inner electrons from one atom to another, either directly or by replacement of the 2 bonding electrons, allowing the latter to enter the inner position in the adjacent atom. It seems that such shifts might readily occur in either way, particularly at high temperatures or during reactions with other molecules.

A conjugated system may be represented by 2 extended octets at the ends of a 4-carbon atom chain. It is likely also that the end atoms are

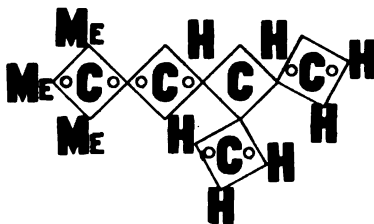


Fig. 5.—*Iso*-dibutylene.

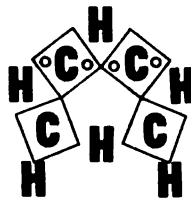
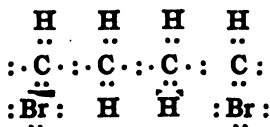
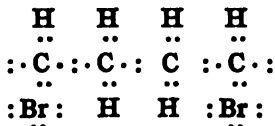


Fig. 6.—Conjugation.

often close together and joined by a loose "hydrogen bond,"<sup>13</sup> as in the formula of Fig. 6. When addition occurs it may then be at the two end carbon atoms, the first addition product being,



Under the influence of the attraction of the bromine atom attached to the remaining extended octet at the end of the chain, the two inner electrons may be assumed to be drawn from the central atom to this one, giving



The next addition will now be on the center atoms.

<sup>13</sup> Rodebush and Latimer, Ref. 3, and Huggins have assumed such bonds. The attraction of 1 hydrogen nucleus by 4 electrons, as discussed in this paper, is a somewhat similar idea.

**Benzene.**—The formation of benzene from acetylene, which is suggestive in connection with the structure of the former, probably consists in the telescoping of 3 molecules of acetylene to form a ring. Either of the structures in Fig. 7 might result from such a reaction, and both appear to be well suited to represent the properties of the substance. Both structures are very symmetrical and compact, and the constraints which apparently would be present should make the molecule unusually rigid and inert, though it must still be unstable on account of the extended octets which are present. Both formulas represent the carbon atoms as being

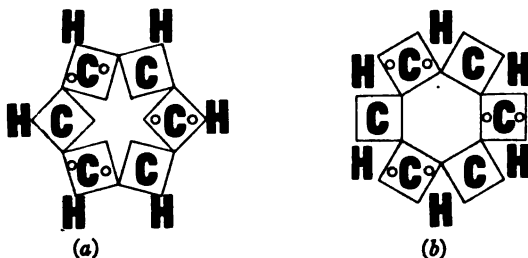


Fig. 7.—Benzene formulas.

in a single plane, and the two *ortho* positions are identical with each other in both. The structure in Fig. 7(b) presents obvious possibilities of reduction to hexamethylene, and of condensed ring formation. Neither reduction nor condensation to naphthalene appears to be as directly possible with rings of the first type, though not necessarily excluded.

The three extended octets are still the more reactive points of the above structures, and when one of the hydrogen atoms of the molecule repre-

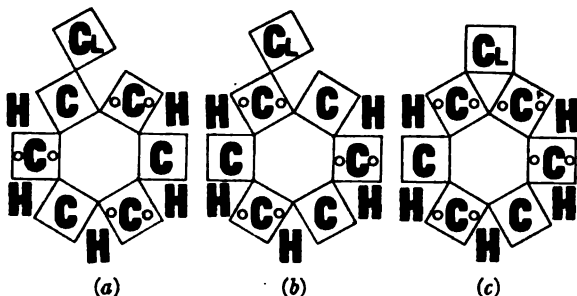


FIG. 8.—Rearrangements in chlorobenzene.

sented in Fig. 7(b), for example, is substituted, the new group will usually be attached to one of them. Following the attachment a subsequent change may or may not occur according to the nature of the substituent. If the latter is a halogen or a singly bonded group, a shift of electrons similar to those assumed in the discussion of conjugation may follow, in this case extending throughout the molecule. As represented in Fig. 8(a) and (b),

the structure first formed goes over to one in which the reactive octets are *ortho-para* to the new group. If, however, it is an extended octet which originally becomes attached to an extended octet of the ring, then apparently the shift of electrons does not occur. The remaining two reactive octets will then be in the *meta* position to the substituted group, and the second addition will be on one of them. The factors determining whether or not the shift postulated above will occur, are perhaps the electro positive or negative character of the group substituted and the size of the octet. The groups strongly attracting electrons will cause the shift, if at the same time an existing distortion of the electron arrangement, due to linkage of octets which are dissimilar in size, is relieved. One or the other or both of these factors are probably operating in the case of the halogens, hydroxyl, or any normal carbon octet. With such groups as  $\text{—CHO}$ ,  $\text{—COOH}$ ,  $\text{—CN}$ , etc., the connecting octet is itself extended according to the present idea, and of approximately the same size as the reactive octets of the ring, so a symmetrical and unstrained connection can be made between the two. The fact that the groups  $\text{—SO}_3\text{H}$  and  $\text{—CF}_3$  direct to the *meta* positions may possibly be regarded as evidence of the importance of the size effect, since in each of these cases the connecting octets are probably considerably larger than the normal carbon octet, though neither is extended in the sense used here.

The preceding considerations apply equally well to either of the two proposed formulas. The following applies chiefly to the one chosen for illustration in Fig. 8. If the latter is assumed, substituted atoms or groups must be attached in the plane of the ring, and probably "cover" rather completely the position originally occupied by the displaced hydrogen atom. In some instances it would seem that the new atom might become attached to two points of the ring, by a telescoping process like that discussed in the ordinary reactions. Fig. 8(c) shows such an attachment of a chlorine atom. Consequences which might be expected to follow this linkage are the increased difficulty of removing a halogen atom from the benzene ring, and second, after three extended octets had been converted by this process to ordinary ones, the reactivity of the molecule with regard to substitution should be largely destroyed. Both of these conclusions may possibly be of service in interpretation of actual phenomena.

**Oxides of Carbon.**—In assigning a structure to carbon dioxide, consideration of its properties in relation to those of substances of analogous composition is particularly important. The formula which seems most satisfactory in this respect is shown in Fig. 9(a). Bearing in mind that elements after the first period cannot in general have the extended grouping, it is clear that a similar representation is possible for carbon disulfide but not for silicon dioxide or silicon disulfide, a distinction which is supported by the actual character of the substances. This experimental

distinction militates strongly against such formulas as that in Fig. 9(b) for carbon dioxide, for if this type of bonding is possible in carbon dioxide or carbon disulfide it is difficult to see why it should not be in silicon dioxide or disulfide. It is therefore assumed in all later applications that 1 atom seldom shares more than 2 electrons with any other 1 atom.

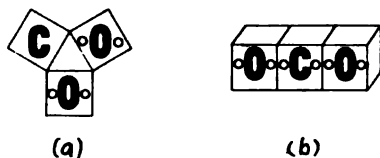


Fig. 9.—Carbon dioxide.

The treatment of ions, or other substances which exist only in polar solvents or polar crystals, constitutes an interesting field in itself which cannot be included here. The possibilities of solvation when in solution, and of complete separation of all the atoms of the solids into charged units of the crystal lattice, may make definite formulation difficult or meaningless in such cases. To show that some of the provisional requirements may be met, however, the reaction of carbon dioxide with oxide ion (and a few later examples) are given. The formula in Fig. 10 for carbonate ion, for

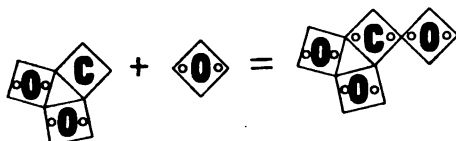
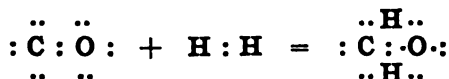


Fig. 10.—Reaction of  $\text{CO}_2$  with oxide ion.

instance, gives a "saturated" structure without addition of further oxide ion, hence orthocarbonate ion will not ordinarily form. The unity of the carbon dioxide group is preserved in this formula, which gives it advantages analogous to those of the Berzelian type for oxygen acids and salts. The breaking of the polar bonds of the ion when it enters a crystal, resulting in the formation of 3 symmetrically placed oxide ions about a central charged carbon atom would satisfy the usual ideas of crystal structure, and so on.

Carbon monoxide is given the formula  $\begin{smallmatrix} \cdot\cdot & \cdot\cdot \\ \vdots & \text{C} & \vdots \\ \cdot\cdot & \cdot\cdot \end{smallmatrix} \text{O}$ . Its reaction with hy-

drogen, yielding formaldehyde, may be written



Other characteristic reactions are those which occur under suitable stimuli with hydrogen chloride, chlorine and ammonia. Since only one molecule of

each of the latter substances ordinarily adds to the carbon monoxide molecule, the resulting compound in each instance is supposed to be of the type indicated in Fig. 11, where the halogen atom has telescoped with both of the extended octets of the carbon monoxide.

**Groups Containing Carbon, Hydrogen and Oxygen.**—The structure of formaldehyde has just been indicated. Its own reactions, condensations,

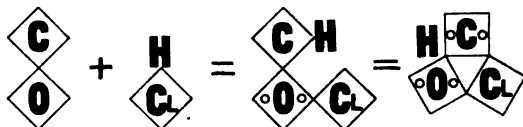


Fig. 11.—Reaction of CO with HCl.

etc., are quite similar in type to those already discussed. Its higher homologs appear to require little comment, other than to point out the possibility that they are to be represented by formulas like one of those for acetaldehyde in Fig. 12. (Compare with acids below.)

Keto-enol tautomerism is an illustration of an equilibrium which requires no change in the basic structure of the reacting molecules, according to the present theory. The group which is present in a 1:3-



Fig. 12.—Acetaldehyde.

diketone, for example, may be represented as in the first formula in Fig. 13. Here the presence of the extended octets on each side of the central  $\text{CH}_2$  group no doubt has a tendency to extend its carbon atom also, rendering the hydrogen nuclei rather labile, and facilitating the exchange pictured in the figure.

The carboxyl group is itself quite polar, and the properties ordinarily assigned as typical are those which it shows in polar solvents. In non-polar media and as vapors, acids usually exist as double molecules. Since the following remarks presuppose the carboxyl structure to be essentially unaffected by solvation or association, they are tentative in character and limited to a few only of the numerous suggestions which occur. Formic acid is represented in Fig. 14(a). Here the 2 hydrogen nuclei are located at opposite sides and slightly outside of the enclosure formed by the other 3 atoms. With the loss of one of the hydrogen ions the remaining one would then be drawn to a position in the center of the entire molecule from which it might be difficult to withdraw it, explaining the monobasicity of the acid. When some radical is attached to the carboxyl carbon, the

symmetry of the molecule is lost and the oxygen-oxygen bond is often broken by the attraction of the radical for one or the other of the oxygen atoms. The various possible stages of separation are shown in Fig. 14(b). The hydrogen ion is thought of as shifting from one loose point of attachment to another, being only a little more firmly held by the extended carbon octet than by the oxygen. These views are in accord with the idea of Lewis that organic acids in general, exist in the form of tautomers, one of which is highly dissociated and one of which is very weak.

**Nitrogen.**—Elementary nitrogen in the present scheme is ( $\ddot{\text{N}}:\ddot{\text{N}}:$ ). The symmetry of this arrangement is of a higher type than in any other unsaturated substance, which perhaps accounts in part for its low ex-

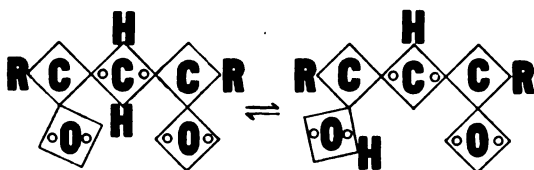


Fig. 13.—Keto-enol tautomerism.

ternal field and small reactivity with respect to polymerization or addition. The formula indicates that nitrogen could actually lose electrons to another element only with the greatest difficulty, but should be able to acquire them, forming nitride ion. In the latter respect it is, as a matter of fact, fairly reactive. The molecule should withstand high temperatures with little dissociation because the extended form is thus favored and because complete octets cannot be formed by the individual atoms. Nitrogen and carbon monoxide are isosteric, in Langmuir's<sup>14</sup> terminology, with each other and with cyanide and acetylide ions.

To take up the individual types of the compounds of nitrogen would unduly extend this discussion and add little new in principle. Numerous

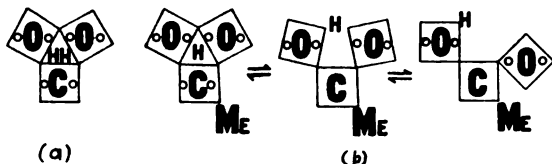


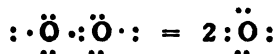
Fig. 14.—Formic and acetic acids.

structures which seem to permit satisfactory interpretation of the facts in this field are readily devised.

**Oxygen.**—The ethylenic character of oxygen appears from the formula ( $\ddot{\text{O}}:\ddot{\text{O}}:$ ). Less symmetrical, it should be more reactive than nitrogen.

<sup>14</sup> Langmuir, *THIS JOURNAL*, 41, 1543 (1919).

Also its dissociation at very high temperatures should be more complete than in the case of nitrogen, for each atom may have an octet as in the equation



In low temperature oxidations, particularly of the very electropositive metals, the formation of the peroxide group or ion,  $:\ddot{\text{O}}:\ddot{\text{O}}:$ , seems a natural consequence of the oxygen structure.

**Boron Compounds.**—The simplest well recognized gaseous hydrides of boron are of the formulas  $\text{B}_2\text{H}_6$ ,  $\text{BH}_3$  and  $\text{B}_2\text{H}_4$ , structures of which are shown in Fig. 15. The last two obviously offer difficulty in representation



Fig. 15.—Hydrides of boron.

by the ordinary theory. It is also interesting to note that  $\text{B}_2\text{H}_6$  substitutes rather than adds halogen. It is therefore saturated in the sense that benzene is, *i. e.*, because the boron atoms are almost completely protected by the outer atoms.

There appear to be no volatile oxides of boron. Metaborate ion,  $\text{BO}_3^-$ , may be given a structure similar to that assigned to carbon dioxide. While the latter does not show as much ability to polymerize as might be expected from its formula,  $\text{BO}_3^-$  apparently does, resulting in such ions as  $\text{B}_4\text{O}_7^-$ , and with a reducing agent,  $\text{B}_4\text{O}_6^-$ . An interesting analogy is presented in the cases of  $\text{BO}_3^-$ ,  $\text{CO}_2$  and  $\text{NO}_3^+$ . The last is present, potentially at least, in  $\text{N}_2\text{O}_4$ . The tendency, like that of carbon dioxide, to add oxide ion should be opposed by the negative charge of the metaborate and assisted by the positive charge of the nitro group. The latter should then not exist in the presence of appreciable quantities of oxide or hydroxide ion, but be completely changed to nitrate ion, and the former should form with some difficulty the orthoborate ion, as is the case.

Brief mention will be made of the boron halides. Boron trifluoride, for example, will be written  $:\ddot{\text{F}}:\ddot{\text{B}}:\ddot{\text{F}}:$ . From this formula it would be pre-

dicted that a suitable octet might telescope with the extended boron atom. This behavior is found with halide ions and with ammonia.

### Summary

In this paper the suggestion is offered that multiple bonding involves

the transfer of two electrons from the inner to the outer shell in one or both of two adjacent atomic kernels, the group of 8 being preserved about each, with 2 jointly held electrons constituting the bond. This hypothesis is sufficient to explain the restricted region of the periodic system in which elements characterized by multiple bond formation occur. To meet requirements imposed by the facts relating to stability, reactivity and free rotation, the electrons of unsaturated octets are assumed to be held in equilibrium positions at greater distances from the nucleus than in the ordinary case, the transfer from the extended position to the usual ones liberating energy. No attractive force between electrons is assumed, and the electron arrangement is taken as cubic, (though subject to distortion).

Upon this basis a mechanism is provided for addition and condensation reactions. Interesting viewpoints are afforded in the study of conjugation, the structure and substitution reactions of benzene, and tautomeric shifts of double bonds. Formulas are illustrated and discussed which represent (more satisfactorily in several cases than other current theories do) many of the properties of chain hydrocarbons, the oxides of carbon, the carbonyl and carboxyl groups, nitrogen, oxygen, and the hydrides and oxygen containing ions of boron.

BERKELEY, CALIFORNIA

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF ARKANSAS]

## THE SOLUBILITY OF POTASSIUM PERMANGANATE IN SOLUTIONS OF POTASSIUM SULFATE AND OF SODIUM, SULFATE

By H. M. TRIMBLE

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Raymond B. Stringfield, in discussing the sodium manganate process for the manufacture of potassium permanganate,<sup>1</sup> points out certain solubility effects which are interesting from both the practical and the theoretical standpoint. In the course of the process potassium permanganate is separated by crystallization from a mother liquor which contains, in addition to permanganate, a small percentage of free alkali and varying quantities of the sulfates, chlorides and carbonates of sodium and potassium. Stringfield says, "Various mixtures of chlorides, carbonates and sulfates are observed to repress the solubility of permanganate greatly, a mother liquor of 3.0% being common, and 1.0% not uncommon, against a normal solubility of potassium permanganate in pure water of 6.0 to 7.0%." These facts suggested an investigation of the solubility of potassium permanganate in solutions of these salts. Sackur and Taegener<sup>2</sup> have determined the solubility in solutions of potassium carbonate, potassium chloride and potassium hydroxide at several temperatures. Their results

<sup>1</sup> Stringfield, *Chem. Met. Eng.*, 22, 1027 (1920).

<sup>2</sup> Sackur and Taegener, *Z. Elektrochem.*, 18, 723 (1912).



at 25° are given in Table III because of their interest in this connection. The values in the case of potassium hydroxide were interpolated from their data. This paper presents data on the solubility of potassium permanganate in solutions of potassium sulfate and of sodium sulfate.

All determinations of solubility were made at 25°. The thermometer used was a standard instrument. Richards and Yngve have shown<sup>3</sup> that a thermometer may be calibrated within a certain temperature range by determining the solubility of sodium sulfate decahydrate at the temperature in question, as read, and correcting to the true temperature at which that solubility is found. The mean of two closely agreeing determinations of the solubility of sodium sulfate decahydrate at 25° as read from this thermometer was 21.802%. The value found by Richards and Yngve, calculated to the same basis, is 21.750%. The error is +0.052%, corresponding to an error in temperature measurement of about +0.04°. The mean of two very careful determinations of the concentration of a solution of potassium permanganate saturated at 25° as read was 7.097%. Interpolation from the results of Baxter, Boylston and Hubbard<sup>4</sup> gives the solubility at this temperature as 7.104%. This difference, -0.007%, corresponds to an error in temperature measurement of about -0.03°. From these experiments it was concluded that the temperature as measured was accurate within the limits of experimental error in the determinations. The thermostat was of the usual electrically heated and regulated type. The temperature varied at most 0.02° from the desired temperature; but in the great majority of runs the temperature control was better than this.

The potassium permanganate, potassium sulfate and sodium sulfate were all an imported product, "for analysis," purchased before the war. Tests showed that the permanganate was free from chloride sulfate and the heavy metals. No oxides of manganese could be detected on dissolving and diluting with conductivity water. Analysis of the sulfates by precipitating and weighing as barium sulfate gave results which agreed with the theoretical values within a few hundredths of 1%. Qualitative tests showed that chlorides and the heavy metals were absent. Flame tests showed that other alkali metals were absent in the sodium sulfate. There was a very slight trace of sodium in the potassium sulfate. The sodium oxalate used in standardizing permanganate solutions was also an imported product prepared especially for that purpose. The other chemicals used were from the ordinary laboratory supply. The hydrogen peroxide used was freed from a small quantity of sulfuric acid which was present by shaking with barium carbonate and filtering. Hydrochloric acid was redistilled to free it from a small amount of the same impurity. Conductivity water was prepared by redistillation; first from alkaline permanganate, then from dil. sulfuric acid, and care was taken to exclude dust and fumes from the laboratory. It was preserved in thoroughly steamed bottles until used.

The method of the investigation followed that of Baxter, Boylston and Hubbard.<sup>4</sup> Stock solutions of the sulfates, saturated at room temperature, were prepared; and solutions of the approximate concentrations desired for the different runs were prepared

<sup>3</sup> Richards and Yngve, *THIS JOURNAL*, 40, 164 (1918).

<sup>4</sup> Baxter, Boylston and Hubbard, *ibid.*, 28, 1336 (1906).

when wanted by diluting these. Two large test-tubes were prepared for each determination by cleaning, steaming out and drying in an oven. A quantity of potassium permanganate crystals was introduced in excess of that necessary for saturation of the solution, and of such size as would pass a 6-mesh screen; then the solution which had been prepared for the run was added, and finally the tubes were sealed before a blast lamp. When it was desired to secure saturation with reference to both permanganate and sulfate, an excess of crystals of each substance was introduced. One tube from each set of two was rotated for 2 hours or longer at  $30^{\circ}$  or above. This was found to produce supersaturation with reference to  $25^{\circ}$  in a few trial runs with sodium sulfate and potassium sulfate solutions of different concentrations. After this supersaturation the temperature of the bath was reduced to  $25^{\circ}$  and held at that temperature. The second tube of each set was then fastened on the rotating device and both were rotated for 6 to 8 hours. A few trials showed that equilibrium could be reached in 4 hours, starting with potassium sulfate solution in contact with permanganate crystals. A longer time was required in the case of sodium sulfate solutions; and the length of time necessary to reach equilibrium was greater the higher the concentration of sodium sulfate. In the runs whose results are given below, excellent agreement was always found between the analysis of the solution in which the equilibrium was approached from supersaturation and that of the solution in which it was approached from undersaturation. After the tubes had been rotated at  $25^{\circ}$  for 6 to 8 hours, they were fastened upright and allowed to remain in this position for 2 hours to permit complete settling. After breaking off the sealed ends of the tubes, portions for analysis were removed by means of pipets or siphon tubes and weighed in small-mouth conical weighing bottles. In somewhat more than half the runs portions were also transferred to pycnometers from each tube and the specific gravity was determined in the usual way. It was not always feasible to work with such large volumes of solution as were required for this.

Sulfates were determined by reducing potassium permanganate with sulfate-free hydrogen peroxide in the presence of a small quantity of hydrochloric acid, also sulfate-free, precipitating as barium sulfate, filtering on Gooch crucibles and igniting and weighing in the usual manner. Occlusion of manganous sulfate or even of sodium or potassium sulfate might occur in this process. The volume of solution at the time of precipitation was always large—about 600 to 700 cc. Occlusion should be lessened by keeping the volume large. A few trial runs in which different quantities of manganous salt were introduced by adding potassium permanganate to sulfate solutions and reducing and analyzing as above gave the correct values for the quantity of sulfate known to be present, within a few hundredths of 1%, in every case. About 20 precipitates from the regular determinations were treated to extract possible occluded manganous salts by fusing with sodium peroxide, adding water, acidifying and adding sulfurous acid to reduce any oxide of manganese which might be present. A few other precipitates were treated by boiling with nitric acid or aqua regia. The solutions were tested for the presence of manganese by heating a small portion with lead peroxide in nitric or sulfuric acid solution. In every case the test for manganese was negative. It is believed that error from occlusion was negligible.

Potassium permanganate was determined by adding an excess of stand-

ard ferrous sulfate solution in the presence of a small quantity of sulfuric acid and titrating back with standard permanganate solution. The

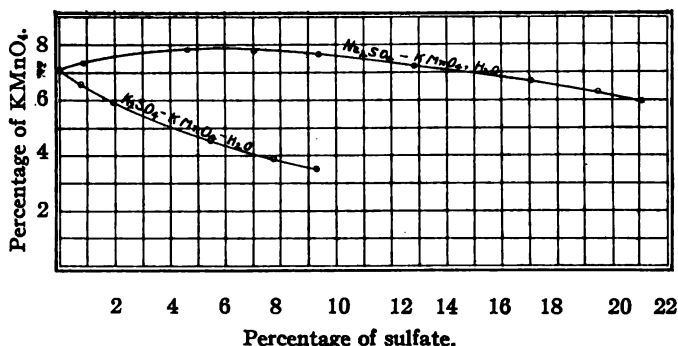


Fig. 1.—Solubility of  $\text{KMnO}_4$  in solutions of  $\text{K}_2\text{SO}_4$  and of  $\text{Na}_2\text{SO}_4$  at  $25^\circ$ .

ultimate standard in this work was sodium oxalate of the highest purity. The data on these determinations are given in Tables I and II. They are also graphically represented in the curves of Fig. 1.

TABLE I

SOLUBILITY OF POTASSIUM PERMANGANATE IN SOLUTIONS OF POTASSIUM SULFATE AT  $25^\circ$

$\text{K}_2\text{SO}_4$ %	$\text{KMnO}_4$ %	Equivalents per liter $\frac{1}{2}\text{K}_2\text{SO}_4$	Equivalents per liter $\text{KMnO}_4$	Parts per 100 parts solvent $\text{KMnO}_4$	Specific gravity $25^\circ/4^\circ$
0.00	7.10	...	0.469	7.64	1.0454
0.80	6.59	0.096	0.437	7.06	1.0483
1.98	5.92	0.239	0.395	6.29	1.0537 <sup>b</sup>
5.47	4.52	0.674	0.307	4.73	1.0730
7.79	3.87	0.972	0.266	4.02	1.0876
9.26 <sup>a</sup>	3.55	1.167	0.247	3.68	1.0979
10.75	0.00	1.340	...	..	1.0864

<sup>a</sup> Saturated in the presence of  $\text{K}_2\text{SO}_4$  and  $\text{KMnO}_4$  crystals.

<sup>b</sup> Calculated.

TABLE II

SOLUBILITY OF POTASSIUM PERMANGANATE IN SOLUTIONS OF SODIUM SULFATE AT  $25^\circ$

$\text{Na}_2\text{SO}_4$ %	$\text{KMnO}_4$ %	Equivalents per liter $\text{Na}_2\text{SO}_4$	Equivalents per liter $\text{KMnO}_4$	Parts per 100 parts solvent $\text{KMnO}_4$	Specific gravity $25^\circ/4^\circ$
0.00	7.10	...	0.469	7.64	1.0454
0.88	7.33	0.131	0.490	7.91	1.0554
4.62	7.83	...	...	8.50	....
7.05	7.75	1.107	0.548	8.40	1.1180
9.34	7.67	...	...	8.31	....
12.85	7.27	...	...	7.84	....
17.05	6.68	...	...	7.16	....
19.43	6.25	3.382	0.489	6.67	1.2363
21.04 <sup>a</sup>	5.91	...	...	6.28	....
21.80	0.00	3.705	...	..	1.2071

<sup>a</sup> Saturated in the presence of  $\text{KMnO}_4$  and  $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$  crystals.

TABLE III  
SOLUBILITY OF POTASSIUM PERMANGANATE IN SOLUTIONS OF POTASSIUM CARBONATE,  
CHLORIDE AND HYDROXIDE<sup>a</sup> AT 25°

Equivalents electrolyte per liter	Equivalents of $\text{KMnO}_4$ per liter in solutions of		
	$\text{K}_2\text{CO}_3$	$\text{KCl}$	$\text{KOH}$
0.1	0.4375	0.4315	...
0.5	....	0.306	...
1.0	0.2589	0.220	0.228 <sup>a</sup>
2.0	....	0.1432	0.153 <sup>a</sup>
4.0	0.093	....	0.102 <sup>a</sup>
6.0	....	....	0.092 <sup>a</sup>
8.0	....	....	0.046 <sup>a</sup>
10.0	....	....	0.032 <sup>a</sup>

<sup>a</sup> Interpolated.

The weights and the volumetric apparatus used throughout all the work were calibrated and the necessary corrections were applied.

The specific gravities of sodium sulfate, potassium sulfate and potassium permanganate solutions of various concentrations were determined at 25°. The pycnometers used were of the Geissler type of 25 and 50 cc. capacity. Each pycnometer was repeatedly calibrated by determining the weight of conductivity water, recently boiled, which was held at 25°. Practically every solution whose specific gravity was determined was analyzed. In a few cases solutions were prepared by diluting weighed

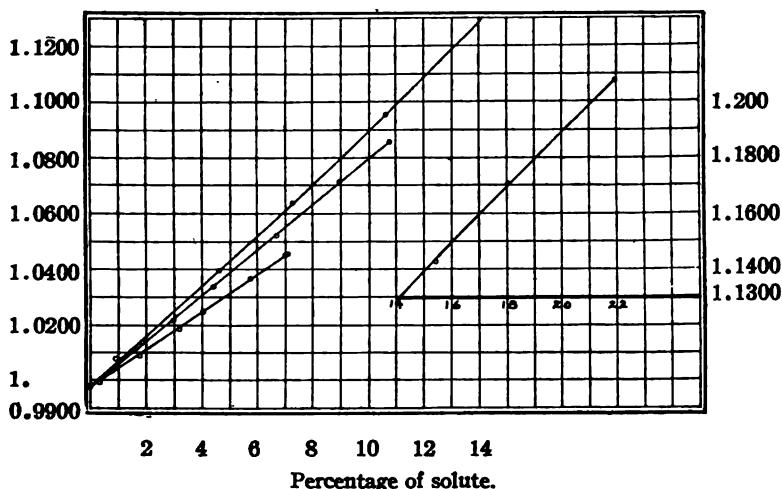


Fig. 2.—Specific gravities of solutions of  $\text{Na}_2\text{SO}_4$ ,  $\text{K}_2\text{SO}_4$  and  $\text{KMnO}_4$  at 25°/4°. The order of curves from left to right is  $\text{Na}_2\text{SO}_4$ ,  $\text{K}_2\text{SO}_4$ ,  $\text{KMnO}_4$  and  $\text{Na}_2\text{SO}_4$ .

quantities of solution of known concentration with known weights of water. The data are given in Tables IV, V and VI and are represented graphically by means of the curves of Fig. 2. All specific gravities are given in terms of that of water at 4° taken as unity.

TABLE IV  
SPECIFIC GRAVITIES OF SODIUM SULFATE SOLUTIONS AT 25°/4°

Na <sub>2</sub> SO <sub>4</sub> %	N	Sp. gr.	Na <sub>2</sub> SO <sub>4</sub> %	N	Sp. gr.
0.88	0.125	1.0079	10.61	1.636	1.0952
1.77	0.252	1.0135	15.44	2.484	1.1425
4.61	0.668	1.0393	18.09	2.981	1.1705
7.28	1.090	1.0638	21.80	3.705	1.2071

TABLE V  
SPECIFIC GRAVITIES OF POTASSIUM SULFATE SOLUTIONS AT 25°/4°

K <sub>2</sub> SO <sub>4</sub> %	N	Sp. gr.	K <sub>2</sub> SO <sub>4</sub> %	N	Sp. gr.
0.76	0.088	1.0033	6.71	0.810	1.0520
2.97	0.348	1.0212	8.97	1.103	1.0712
4.44	0.527	1.0335	10.75	1.340	1.0864

TABLE VI  
SPECIFIC GRAVITIES OF POTASSIUM PERMANGANATE SOLUTIONS AT 25°/4°

KMnO <sub>4</sub> %	N	Sp. gr.	KMnO <sub>4</sub> %	N	Sp. gr.
0.30	0.019	0.9992	5.72	0.375	1.0368
1.77	0.113	1.0089	7.01	0.464	1.0451
3.20	0.206	1.0186	7.10	0.469	1.0454
4.05	0.263	1.0245	..	...	....

Normality is stated in the above tables in terms of  $\frac{1}{2}$  Na<sub>2</sub>SO<sub>4</sub>,  $\frac{1}{2}$  K<sub>2</sub>SO<sub>4</sub>, and KMnO<sub>4</sub>, respectively.

W. C. Mc. Lewis<sup>1</sup> points out that the specific gravities of aqueous solutions may be represented fairly closely by an expression of the form,  $S = S_0 + ac + bc^2$ , where  $S$  is the specific gravity of the solution,  $S_0$  is the specific gravity of the solvent at the temperature of experiment,  $c$  is the concentration of the solute in any convenient units, and  $a$  and  $b$  are constants determined by experiment. That portion of the above expression,  $ac + bc^2$ , which gives the increase in specific gravity for the particular solution and concentration over the specific gravity of water, may be derived from the specific-gravity curve for the solution by subtracting the specific gravity of water from the specific gravity for a given concentration as read from the curve. If the law holds for solutions containing two or more salts, the specific gravities of such solutions should be given by the expression,  $S = S_0 + (ac + bc^2)_1 + (ac + bc^2)_2 + \dots$ , where the increases in specific gravity are given for each of the salts at their particular concentrations by  $(ac + bc^2)_1$ ,  $(ac + bc^2)_2$ , etc. The different values here indicated were found and summed up in an attempt to supply the missing values for the specific gravities of the solutions tabulated in Tables I and II. The method gives good results in the solutions containing potassium sulfate and potassium permanganate, as will be seen from Table VII.

<sup>1</sup> Lewis, "A System of Physical Chemistry," Longmans, Green and Co., 1920, vol. I, p. 210.

TABLE VII

COMPARISON OF CALCULATED AND ACTUAL VALUES FOR THE SPECIFIC GRAVITIES OF SOLUTIONS CONTAINING POTASSIUM SULFATE AND POTASSIUM PERMANGANATE

$K_2SO_4$ %	$KMnO_4$ %	Calc.	Sp. gr.	Found
0.80	6.50	1.0487		1.0485
1.98	5.92	1.0537		....
5.47	4.52	1.0728		1.0730
7.79	3.87	1.0873		1.0876
9.26	3.55	1.0972		1.0979

The value for the specific gravity of the solution containing 1.98% of potassium sulfate and 5.92% of potassium permanganate as calculated was inserted in Table I. The attempt to calculate the specific gravities of solutions containing potassium permanganate and sodium sulfate failed in those cases where specific gravities had been determined, the values turning out lower than those found by experiment. The difference between calculated and actual results becomes rapidly greater as the concentration of the solution increases. Since metathesis occurs in this case, resulting in the formation of new substances in unknown quantities, this failure was to be expected.

Finally, three determinations of the solubility of potassium permanganate in solutions containing known concentrations of sodium sulfate and potassium sulfate were made in an attempt to discover the specific effect upon the solubility of potassium permanganate in a solution of either sulfate produced by adding the other. The saturation of solutions was carried out as above, even a longer time being allowed for reaching equilibrium. The concentrations of potassium sulfate and of sodium sulfate in the original solutions being known, the final analysis was for the determination of the permanganate content only. From the data thus secured the concentrations of the constituents of the final solutions were calculated. It was assumed that the excess permanganate crystals did not appreciably adsorb the sulfates present. The data are given in Table VIII.

The values of the first line under "Specific Effects" were calculated as follows. If we take as solvent the solution of sodium sulfate which contains the relative proportions of salt and water given in Cols. 2 and 4 of Line 1, under "Constituents" we have a solution containing 6.24% of sodium sulfate. Plotting the values of Table II, Col. 5, against the corresponding concentrations of sodium sulfate in percentages of the solution chosen as solvent and reading from the curve, it is found that a solution of this concentration will dissolve 8.48 parts of potassium permanganate per hundred parts of solvent. Calculating again from Line 1 of Table VIII, it is found that when 5.00 parts per hundred of potassium sulfate are added to the solvent the solubility of permanganate is reduced to 5.33 parts per hundred, a

decrease of 3.15 parts per hundred. The other values were calculated in the same manner. Within the limits covered by these experiments, potassium sulfate acts powerfully to decrease the solubility of potassium permanganate in solutions of sodium sulfate. The effect of sodium sulfate in increasing the solubility in solutions of potassium sulfate is much smaller. The work had to be discontinued at this point, so that no further determinations in this series could be made.

TABLE VIII

SOLUBILITY OF POTASSIUM PERMANGANATE IN SOLUTIONS OF POTASSIUM AND SODIUM SULFATES AT 25°

Constituents of Solutions			
$K_2SO_4$ %	$Na_2SO_4$ %	$KMnO_4$ %	$H_2O$ %
4.53	5.66	4.83	84.98
5.73	3.34	4.40	86.53
6.77	1.32	4.03	87.88

SPECIFIC EFFECTS ON SOLUBILITY OF POTASSIUM PERMANGANATE IN PARTS PER 100 PARTS OF THE SOLUTION CHOSEN AS SOLVENT

In $Na_2SO_4$ Solution				
$Na_2SO_4$ %	Normal solubility	$K_2SO_4$ introduced	Solubility	Decrease
6.24	8.48	5.00	5.33	3.15
3.72	8.38	6.38	4.90	3.48
1.48	8.01	7.59	4.52	3.49

In $K_2SO_4$ Solution				
$K_2SO_4$ %	Normal solubility	$Na_2SO_4$ introduced	Solubility	Increase
5.06	4.97	6.32	5.40	0.43
6.21	4.56	3.62	4.77	0.21
7.15	4.25	1.39	4.26	0.01

There is, as yet, no theory upon the basis of which the effect of one very soluble electrolyte upon the solubility of another of the same nature can be quantitatively predicted. Harkins<sup>6</sup> shows that in the case of a uni-univalent salt of moderate solubility the solubility of the salt is reduced by the addition of an electrolyte which gives a common ion, the curves showing a regular decrease in solubility of the saturating salt as the concentration of the added salt increases. All the curves fall in a limited and well defined group. Curves for salts with a solubility in water up to about one equivalent per liter fall in this group,<sup>7</sup> the curves falling higher and higher in the group as the solubility in pure water increases. The case of the solubility of potassium permanganate in any solution where a common ion is present comes under this rule, since its solubility in pure water at 25° is 0.469 equivalent per liter. When the curve for the solubility of

<sup>6</sup> Harkins, THIS JOURNAL, 33, 1854 (1911).

<sup>7</sup> Ref. 6, p. 1859.

potassium permanganate in solutions of potassium sulfate is plotted, using the same units which Harkins uses, it is found to lie in the upper part of the characteristic group. The curves representing the solubility of this salt in solutions of potassium carbonate, potassium chloride and potassium hydroxide fall quite close to that representing its solubility in solutions of potassium sulfate. All these solubility curves are such as would be expected from a qualitative application of the solubility product principle.

The form of the curve for the solubility of potassium permanganate in solutions of sodium sulfate is unusual. In general, the effect of an electrolyte which does not give a common ion is to increase the solubility of the saturating salt, as a result of metathesis, whatever the concentration of the added electrolyte. Here the effect in increasing the solubility rises to a maximum at about 6% of sodium sulfate as the concentration of this salt increases. At higher concentrations of sodium sulfate, however, the effect is just reversed. A like effect is found in some other cases. The curves for the solubility of calcium sulfate in solutions of magnesium chloride, of sodium chloride and of sodium nitrate, for example, pass through such a maximum. For the form of such curves there seems to be no satisfactory explanation.

The mother liquors from which potassium permanganate is crystallized contain very large percentages of sodium salts, but only small percentages of potassium salts other than the permanganate. Sodium carbonate and sodium chloride have solubilities in water of the same order of magnitude as that of sodium sulfate. Two of these three salts will practically always be present in the mother liquors; and all three may be present. The particular salts present and their concentrations will depend upon the procedure which is being followed. It is difficult to account for the low concentrations of permanganate in the mother liquors which Stringfield reports, unless some such effect as that which has been found here in connection with concentrated solutions of sodium sulfate is responsible.

### Summary

This paper reports the results of a study of the solubility of potassium permanganate in solutions of potassium sulfate and of sodium sulfate at 25°, and gives data on the specific gravities of solutions of sodium sulfate, potassium sulfate and potassium permanganate at the same temperature. The solubility of potassium permanganate in solutions of potassium sulfate decreases with increasing concentration of sulfate. In solutions of sodium sulfate the solubility of this salt increases with increasing concentration to a maximum in solutions containing about 6% of sodium sulfate; then there is a slow decrease in solubility to a minimum in solutions which contain the maximum quantity of the salt which can go into solution in the presence of potassium permanganate crystals. For the lower concentrations of each



sulfate, potassium sulfate acts powerfully to decrease the solubility of potassium permanganate in solutions of sodium sulfate, while sodium sulfate increases its solubility in solutions of potassium sulfate to a much smaller degree.

FAYETTEVILLE, ARKANSAS

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF COLORADO]

## ADSORPTION OF IODINE BY SILVER IODIDE

BY FRANK E. E. GERMANN AND RALPH N. TRAXLER

Received July 25, 1921

On page 98 of Bancroft's "Applied Colloid Chemistry,"<sup>1</sup> we find the following statement:

"Carey Lea<sup>2</sup> has shown that silver iodide adsorbs iodine strongly. This property of silver iodide was verified by shaking portions of freshly precipitated and still moist AgI with iodine solutions. An alcoholic solution of iodine, diluted until it has a pale sherry-wine color is quickly decolorized by AgI and the same thing happens with a very dilute solution of iodine in KI which in a few minutes becomes as colorless as water. It is probably this adsorption which makes silver iodide photographic emulsions apparently less sensitive than the silver bromide emulsions. If so, it should not be difficult to overcome this trouble."

Experiments were performed to determine whether adsorption did take place. Acetone, water-free methyl alcohol, 95% ethyl alcohol, and a water solution of potassium iodide were used as solvents for the iodine, which was purified several times by grinding with potassium iodide and then subliming. Standardized sodium thiosulfate solution (1 cc. = 0.0023 g. of iodine) was used for titration. Silver iodide was made by precipitating from solutions of potassium iodide and silver nitrate of strength ranging from *M* to 0.1 *M*. The potassium iodide and silver nitrate used were purified by recrystallization. All experiments were performed in a room with no actinic light present.

In the first series of experiments the precipitated silver iodide made from *M* solutions of silver nitrate and potassium iodide was thoroughly washed, dried and passed through a 100-mesh screen, in order to have fairly uniform particles. In each of these experiments 0.2 g. of dry, powdered silver iodide was added to 25 cc. of the solvent containing 0.05 g. of the purified iodine. The container was stoppered and the mixture shaken for 1 minute, 5, 10, 15, 20 and 30 minutes. Care was taken not to increase the temperature appreciably while shaking. The mixture was filtered rapidly by suction, and the filtrate titrated with sodium thiosulfate solution for free

<sup>1</sup> Bancroft, "Applied Colloid Chemistry," McGraw Hill Book Co., 1921.

<sup>2</sup> *Am. J. Sci.*, [3] 33, 492 (1887); See also Problem 54 of Bancroft's "Research Problems in Colloid Chemistry." Nat. Research Council Reprint No. 13, 1921.

iodine. In none of the experiments was an adsorption of iodine noted, within a low limit of experimental error.

Experiments using the same kind and quantities of material were made, and the mixture was boiled for 15 minutes to 1 hour under a reflux condenser at a pressure of 62 cm. of mercury. These upon being filtered and titrated showed no decrease in iodine content.

Several very dilute solutions of iodine (about 0.01 g. in 25 cc. of solvent) were run qualitatively with amounts of silver iodide larger than 0.2 g. No decolorization of the iodine was noted. Also, several determinations were made in the presence of actinic light, but no iodine was removed by such a procedure.

Silver iodide was then made from the same strength of solutions and thoroughly washed with distilled water, but added to the iodine solutions without being dried. This conformed with the former experimenter's "freshly precipitated still moist silver iodide." Still there was no decolorization of the iodine solutions.

Another series of experiments was run using silver iodide made from approximately 0.1 *M* solutions of potassium iodide and silver nitrate. A very slight excess of potassium iodide was used in the precipitation, which caused the formation of a fine, almost colloidal silver iodide. This was filtered with a great deal of difficulty, washed thoroughly with water, very dil. ammonia and water and then with very dil. nitric acid followed by distilled water.<sup>3</sup> The freshly precipitated, moist, thoroughly washed silver iodide was added to a sherry-wine red solution of iodine in 95% alcohol. No decolorization of the solution could be detected.

Next a series of experiments was run using silver iodide precipitated as above except that a very slight excess of silver nitrate was used instead of an excess of potassium iodide. The excess of silver nitrate or of potassium iodide in either case was not over 1%. The silver iodide precipitated by this method settled more readily than that made with a slight excess of potassium iodide and was more easily filtered. The precipitate was washed by decantation with water, ammonia and nitric acid followed by water, then filtered by suction. Various amounts were added to a sherry-wine red solution of iodine in ethyl alcohol with very slight decolorization.

In searching for a reason for the complete decolorization of the solutions of the former experimenter it was noted that no mention was made in his work of any washing of the silver iodide. More silver iodide was made from *M* solutions of potassium iodide and silver nitrate using a 10% excess of silver nitrate, but was filtered upon a Büchner filter without any washing, thus leaving any adsorbed or occluded silver nitrate in the precipitate. When approximately 1.0 g. (calculated dry) of this moist, unwashed silver iodide was added to 25 cc. of solvent containing 0.05

<sup>3</sup> Lottermosser and Rothe, *Z. physik. Chem.*, **62**, 363 (1908).

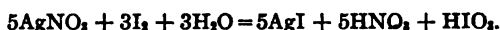
g. of iodine, shaken for 30 seconds and filtered, 0.02 g. of the iodine disappeared. Approximately 3.0 g. of this silver iodide in a similar solution removed all the free iodine, leaving a water-white solution.

Silver iodide was also made by precipitating from dil. solutions of potassium iodide and silver nitrate (approximately 0.1 *M*) using a 10% excess of silver nitrate. The precipitate was filtered upon a Büchner filter without washing and it was found that about 1 g. of the moist silver iodide decolorized a sherry-wine red solution of iodine in ethyl alcohol. The precipitate was washed with 250% of its own weight of water by suction on the Büchner filter and still it was found that 1.5 g. of it would decolorize a sherry-red solution of iodine. After washing with 500% of water in the same way, 2 g. of the silver iodide was required to effect complete decolorization.

The same experiments using unwashed silver iodide precipitated both from conc. and dil. solutions of potassium iodide and silver nitrate and using 10% excess of silver nitrate were tried upon a sherry-red solution of iodine in potassium iodide-water solution. About 3.5 g. of silver iodide precipitated from the concentrated solutions was required to effect complete decolorization of such a solution of iodine. Silver iodide precipitated from more dilute solutions decolorized the iodine solutions more easily, due to the greater amount of silver nitrate adsorbed by the finer precipitate and the greater quantity of solution held by the greater porosity. The same experiments on washing the precipitate upon the filter were tried in this case and a gradual decline of the decolorizing power of the silver iodide noted with increased amount of washing.

From the results of these experiments using unwashed silver iodide it was concluded that the silver iodide of the former experimenter must not have been washed free from the silver nitrate. Such a conclusion led to the belief that a chemical reaction and not adsorption caused the complete decolorization of Carey Lea's solutions.

When the silver iodide was unwashed there was undoubtedly silver nitrate occluded in the flocculent precipitate. Also there was silver nitrate adsorbed by the silver iodide, which could not be removed without considerable washing. The silver nitrate from both of these sources when added to the iodine solutions in alcohol and to the iodine in potassium iodide reacted with them destroying the color of free iodine. The reaction between silver nitrate and iodine is set forth by V. E. Pavlov and S. D. Shein<sup>4</sup> as follows.



This reaction occurs when there is an excess of iodine present.

We must remember that there is nothing quantitative in Carey Lea's pub-

<sup>4</sup> Pavlov and Shein, *J. Russ. Phys. Chem. Soc.*, 39, 943-7 (1907); *C. A.*, 2, 772 (1908).

lication on this subject, so that we have no way of checking him absolutely.

Some substances such as wood- and blood-charcoal adsorb great quantities of material from solutions, and by their use we are able to remove practically all coloring matter from impure sugar solutions. This, however, is rather the exception than the rule. For example, Lottermosser and Rothe,<sup>5</sup> studying the adsorption of silver nitrate and potassium iodide by silver iodide used from 0.23 to 0.93 g. of silver iodide in 25 cc. of potassium iodide solutions, obtaining values of the adsorption of the order of 0.009 millimol per gram of adsorbent. The solution in equilibrium still contained 0.075 millimol in the 25 cc. In the case of the adsorption of silver nitrate, the maximum adsorption noted was 0.005 millimol per gram when there still remained 0.350 millimol in the 25 cc. The greatest percentage change in composition takes place in the case of the most dilute solutions, being in Lottermosser and Rothe's case 56% as a maximum. The same general results have been obtained by one of us<sup>6</sup> in the case of the adsorption of radium by barium sulfate.

A sherry-wine colored iodine solution contains approximately 2 g. of iodine per liter or about 0.008 millimol per cc. Had Carey Lea used 1 g. of silver iodide in 25 cc. of solution and obtained complete decolorization he would have had 0.2 millimol per gram adsorbed. This value not only seems very large, but also very improbable, since complete adsorption would certainly require a great mass of silver iodide.

It should also be noted that any adsorbed material is efficiently removed only by washing by decantation, as was done by us in order to remove the silver nitrate from the silver iodide. As has been shown, washing on a Büchner funnel removes adsorbed substances only very slowly.

Since Lea used a colorimetric method and hence could make no error on the resulting iodine content, we must conclude that the resulting solution was as "colorless as water." It thus would seem that some chemical reaction rather than adsorption should be taken as the explanation of the decolorization.

In view of the possible experimental error in the procedures used, it may be stated that there is no adsorption of iodine in solutions of acetone, water-free methyl alcohol, 95% ethyl alcohol, and a water solution of potassium iodide, by silver iodide above a maximum limit of 0.02 millimol per gram of silver iodide. Carey Lea claimed to have obtained a rapid and complete decolorization of sherry-wine colored solutions of iodine. The present experiments show conclusively that not sufficient adsorption takes place to cause a change in color of any such magnitude. If there is an adsorption it must be below the limit above stated.

<sup>5</sup> Lottermosser and Rothe, Ref. 3, p. 359.

<sup>6</sup> Germann, "Adsorption of Radium by Barium Sulfate," *THIS JOURNAL*, **43**, 1615 (1921).

### Summary

1. Carey Lea's experiments indicated that iodine was strongly adsorbed from solution by silver iodide.

2. Dry, thoroughly washed silver iodide precipitated from *M* solutions of silver nitrate and potassium iodide was added to alcoholic and potassium iodide water solutions of iodine with no decolorization. Varying lengths of time of agitation and various conditions were tried with no appreciable adsorption.

3. Likewise, moist silver iodide precipitated from *M* and from 0.1 *M* solutions and washed with ammonium hydroxide and nitric acid by decantation was added to similar solutions with negative results.

4. Decolorization was obtained with unwashed silver iodide precipitated both from *M* and from 0.1 *M* solutions, using an excess of silver nitrate. The decolorization was due to a chemical reaction between the iodine in solution and the silver nitrate occluded in the silver iodide and adsorbed upon its surface.

5. Unwashed silver iodide precipitated from dilute solutions of silver nitrate and potassium iodide decolorized the iodine solutions most easily, due to the greater adsorption of silver nitrate by the silver iodide and the larger quantity of solution held because of the increased porosity.

6. A sherry-wine red solution of iodine contains about 0.008 millimol per cc. From the above experimental work it may be concluded that there is no adsorption of iodine from solution by silver iodide above a maximum limit of 0.02 millimol per gram of silver iodide. Hence, if Carey Lea worked with 25 cc. of sherry-wine colored iodine solution containing 0.2 millimol he must have added well over 10 g. of silver iodide to obtain anywhere near complete decolorization.

7. The above results point to the probability that Carey Lea was dealing with a chemical rather than an adsorption phenomenon.

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[CONTRIBUTION No. 4 FROM THE RESEARCH LABORATORY OF THE NATIONAL BISCUIT COMPANY]

### FURTHER STUDIES OF THE PHYSICAL CHARACTERISTICS OF GELATIN SOLUTIONS

BY CLARKE E. DAVIS AND EARLE T. OAKES

Received August 5, 1921

In a previous article<sup>1</sup> an investigation of the viscosity of solutions of various gelatins at 25° was reported.

The present paper covers an investigation of the following properties of gelatin solutions: (1) density~temperature 0-60°; (2) density~concentration at 40°; (3) transition point of gel-to-sol; (4) viscosity~

<sup>1</sup> Davis, Oakes and Brown, *THIS JOURNAL*, **43**, 1526 (1921).

concentration at 40°; (5) viscosity~temperature; (6) viscosity~hydrogen-ion concentration at 40°.

The methods of determining densities, viscosities, and hydrogen-ion concentrations were the same as described in the previous article except that in this work all values for hydrogen-ion concentration were determined both by indicators and by the hydrogen electrode. This was done because in certain ranges of hydrogen-ion concentration, notably around  $P_H$  4 to  $P_H$  5 and above  $P_H$  9, the indicators are unreliable. Both methods were used because it was desired to determine the accuracy of the indicators. Outside the ranges above noted we found little difficulty in checking the hydrogen electrode within  $P_H \pm 0.1^\circ$ . Variations of as much as  $\pm 0.3$  or  $\pm 0.4$  in the value  $P_H$  may be experienced with gelatin solutions at  $P_H$  4 to  $P_H$  5 and above  $P_H$  9. Solutions were made up according to weight per cent. concentration, and only hydrochloric acid and sodium hydroxide were used to alter the values of hydrogen-ion concentration.

Throughout the entire course of this work one sample of hide gelatin was used. This gelatin will be known as 3B and is of as high a grade as we have been able to find. The following table shows its characteristics.

TABLE I  
PROPERTIES OF GELATIN 3B

$P_H$	Moisture %	Ash %	Jell strength at 21° Original $P_H = 4.9$	Absolute viscosity in c. p. of 1% sol. $P_H$ 3.5 at 25°	
				Age Hr. min.	Viscosity
4.9	9.03	0.51	1025	1 20	3.08
				1 30	3.15
				2 0	3.37
				4 15	4.46

It will be noted that while Loeb<sup>2</sup> uses so called iso-electric gelatin which is practically ash free, the gelatin employed by the present authors contains about 0.5% of ash. Owing to the fact that in washing out the salts the more soluble (more hydrolyzed) portions of the gelatin are also washed away and the composition of the gelatin changed, and since the effects of various salts have been investigated by Loeb and found to be small in comparison with the quantities here determined we considered it best to use the gelatin as indicated.

#### Variation of Density with Temperature

One per cent. solutions of 3B gelatin at  $P_H$  8.0 were investigated over a range of from 0° to 60°. As stated in a previous contribution<sup>1</sup> the density of gelatin solutions is affected but little by changes in hydrogen-ion concentration and the character of the gelatin has practically no effect upon

<sup>2</sup> Loeb, *J. Gen. Physiol.*, 1918-21.

the density. In Fig. 1 the density results have been plotted along with the densities of pure water over the same range. From this figure it is seen that the density changes of 1% gelatin solutions parallel those of pure

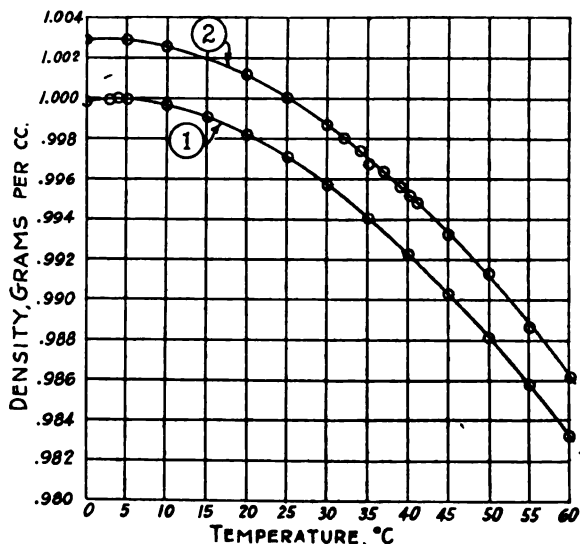


Fig. 1.—Variation of density with temperature, 1 = water, 2 = 1% solutions of 3B gelatin,  $P_H = 8.0$ .

water over the range 0–60°, and may be represented by the formula  $D_g = D_w + 0.00290$  where  $D_g$  is the density of 1% gelatin solution and  $D_w$  is the density of pure water at the same temperature.

#### Variation of Density with Concentration at 40°

The densities of 1, 5 and 10% concentrations of 3B gelatin at  $P_H$  8.0 were determined at 40° and were found to be 0.9954, 1.0067, and 1.0210, respectively.

These results, plotted in Fig. 2, show that the density is a straight line function of the concentration and may be represented according to the formula,  $D_g = D_w + X \times 0.00290$ , where  $D_g$  is the density of gelatin solution,  $D_w$  the density of water and  $X$  the percentage of gelatin. Since the constant at 40° is the same as at all other temperatures between 0° and 60° this is a perfectly general formula for the density of gelatin solutions at any temperature between 0° and 60°. Concentrations of this gelatin greater than 10% could not be used at 40°, and at 25°, 1% solutions jellied in 3 hours.

#### Transition Point of Gelatin

The fact that gelatin solutions increase in viscosity with aging of solution at 35° while at 40° the viscosity is constant indicated a method of

locating the transition point rather accurately. C. R. Smith,<sup>3</sup> in an article "The Mutarotation of Gelatin and its Significance in Gelation" has pointed out the probability of the existence of two forms of gelatin. Smith was led to his belief by polariscopic investigations while our viscosity determinations led us to the same conclusions. Smith did not attempt to locate definitely this transition point: Sol form A  $\rightleftharpoons$  Gel form B, but placed it somewhere between 33° and 35°. In order to study the behavior of the two forms at 35°, two 1% solutions of 3B Gelatin of  $P_H$  4.9 and 7.8, respectively were prepared and each was divided into two parts, "A" and "B." A samples were placed immediately in the thermostat at 35°, while the B samples were placed in the ice-chest for 1 hour and then removed and placed in the thermostat along with the A samples. Both samples of B had formed a solid jelly when they were removed from the ice-chest. The viscosity results obtained on these 4 samples are plotted in Fig. 3. The viscosities of both solutions at  $P_H$

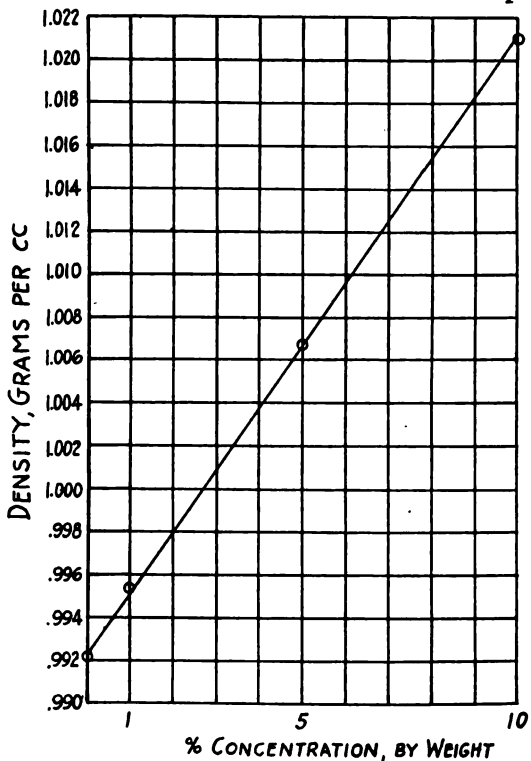


Fig. 2.—Variation of density with concentration; solutions of 3B gelatin at 40°,  $P_H = 8.0$ .

4.9 remained constant, Sample B giving a higher viscosity than A due to the portion of gelatin which had gone over into the gel form. Since the viscosity at  $P_H$  4.9 changes rather slowly with age it was expected that near the transition point the change might be too slow to manifest itself in a short time. The fact that Sample B did not change in viscosity shows that while the gradient is not great enough to cause gel to form in A, neither is it great enough to cause more to form in B, or if 35° is above the transition point to destroy the gel already formed. In other words the change at this hydrogen-ion concentration is too slow to measure. Of the two samples at  $P_H$  7.8, B kept increasing in viscosity, showing that in the hour during which it was in the ice-chest

<sup>3</sup> Smith, *THIS JOURNAL*, 41, 135 (1919).



not all of it had reverted to the gel form and this change continued to take place at  $35^{\circ}$ . The transition point must then be above  $35^{\circ}$ . The A sample of this set behaved exactly like a solution in a state of suspended transformation in that the viscosity remained constant for nearly 4 hours and then increased at about the same rate as did that of the B sample. It is evident from this, then, that the transition point is above  $35^{\circ}$  and that alkali catalyzes the transition. Since it was found that at  $40^{\circ}$  the solutions did not increase in viscosity this work was repeated at  $40^{\circ}$  in exactly the same way except that 2 samples of B were investigated. Sample

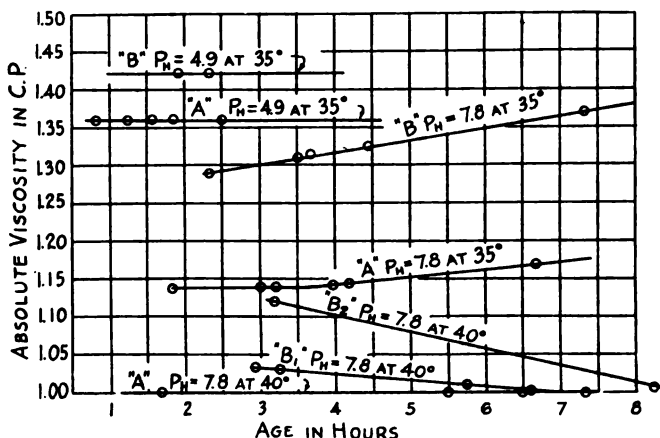


Fig. 3.—Variation of viscosity with age; 1% solutions of 3B gelatin,  $P_H$  4.9 and 7.8 at  $35^{\circ}$  and  $40^{\circ}$ .

$B_1$  was left in the ice-chest for 1 hour and  $B_2$  was left 2 hours. Both  $B_1$  and  $B_2$  were solid jellies when removed from the ice-chest. The results plotted in Fig. 3 show that while the viscosity of Sample A remained constant, those of  $B_1$  and  $B_2$  decreased continually and uniformly until the viscosity was the same as that of the A sample. This then definitely establishes the transition point as between the limits of  $35^{\circ}$  and  $40^{\circ}$ . It is also interesting to note that it requires only a small amount of the gel form B to transform the solution into a solid jelly.

In order to locate the transition point definitely a 4% solution of 3B gelatin was made up to  $P_H$  8.0. This increased concentration was chosen in order to bring out smaller changes than a 1% solution would show. This sample was divided into 3 parts.  $B_1$  and  $B_2$  were put in the ice-chest for 1 and 2 hours respectively, when they were removed and placed in the thermostat at the temperature indicated in Table II. The viscosity is given in seconds rather than in absolute units since it is only the point at which the viscosity just ceases to change with age that we are trying to locate. A was not cooled below  $38^{\circ}$ .

TABLE II  
 VISCOSITY OF 4% SOLUTIONS OF 3B GELATIN,  $P_H$  8.0, AT TEMPERATURES NEAR THE  
 TRANSITION POINT

Temp. °C.	Time	Elapsed time between runs Min.	Viscosity in seconds
Solution A			
38.0	11:25		312.8 <sup>a</sup>
38.0	11:45	20	313.8 <sup>a</sup>
38.0	12:05	20	315.0 <sup>a</sup>
Solution B <sub>1</sub>			
38.0	11:18	..	344.7 <sup>b</sup>
38.0	11:33	15	346.9 <sup>b</sup>
38.0	11:52	19	348.0 <sup>b</sup>
38.2	2:20	148	342.1 <sup>b</sup>
38.2	2:30	10	341.8 <sup>b</sup>
38.2	3:25	55	337.5 <sup>b</sup>
38.2	3:35	10	337.2 <sup>b</sup>
Solution B <sub>2</sub>			
38.1	3:56	..	410.7 <sup>a</sup>
38.1	4:07	11	408.4 <sup>a</sup>
38.1	4:18	11	407.7 <sup>a</sup>

Time for water for No. 2 viscometer (a) at 38° = 59.2 sec.

Time for water for No. 4 viscometer (b) at 38° = 59.8 sec.

It is obvious from Table II that the transition point of gelatin, Sol form A  $\rightleftharpoons$  Gel form B, lies between 38° and 38.1°. A close inspection of the results shows that the transition point is nearer 38.0° than 38.1°. By interpolation the value 38.03° is obtained. It is interesting to note that 4% solutions do not exhibit the lag in the transformation noted in the case of 1% solutions. Smith<sup>3</sup> has also pointed out that the more concentrated solutions come to equilibrium more quickly than the more dilute solutions. It should also be noted that the more of the gel form present the more rapid the increase in viscosity below the transition point and the more rapid the decrease above this temperature.

Another factor liable to affect the determination of the transition point is hydrolysis with its consequent lowering of viscosity. At certain hydrogen-ion concentrations, namely, in very acid or very alkaline solutions, even at ordinary temperatures this factor is quite evident.

With decreasing acidity or alkalinity the temperature must be raised to induce hydrolysis. The question of hydrolysis is entirely separate from the one of transition point and is mentioned only because it is so often confused with the latter. If, at a given temperature and in the absence of the gel form, a decrease in viscosity with age is noted we are evidently dealing with hydrolysis. It is evident from the results described at 40° and at  $P_H$  7.8 no hydrolysis is apparent and the results herein described are free from such effects.

Since gelatin above the transition point is in the soluble form it is inter-

esting to speculate on the physiological significance of this transition temperature  $38.03^{\circ}\text{C}$ . or  $100.5^{\circ}\text{F}$ .

### Determination of Viscosity of Gelatin Solutions at Temperatures below the Transition Point<sup>4</sup>

Since it is only when gelatin solutions reach a temperature below the transition point that the viscosity begins to increase with age, we have modified the procedure for determining the viscosity of gelatin solutions as described in a previous article. This change consists in reheating the solution to  $50^{\circ}$  after filtering and then immediately placing the solution in the thermostat at the desired temperature and stirring vigorously until the temperature of the thermostat is reached. The age is then reckoned from the moment the solution registers  $38.03^{\circ}$ . This change in procedure eliminates the last obstacle to securing exact checks by different workers.

### Variation of Viscosity with Concentration at $40^{\circ}$

As has been pointed out in a previous article<sup>1</sup> the viscosity-concentration formulas so far proposed do not hold for gelatin solutions at  $25^{\circ}$ . Owing to the fact that the gelation factor is different for each gelatin and at each hydrogen-ion concentration it was found quite impossible to apply any such formulas. Furthermore, gelation does not take place at a uniform rate, but the solution may exist for some time in a state of suspended transformation, thus rendering unreliable the application of a formula containing a factor covering the gelation effect. Evidences of this state of suspended transformation were apparent at the time of publication of the earlier paper but were not confirmed until the completion of that part of the present paper dealing with transition point.

In order to test the application of the various viscosity-concentration formulas to gelatin solutions in which the gelation factor was absent, the viscosities of solutions of varying concentrations of gelatin at  $P_{\text{H}}$  8.0 were investigated at  $40^{\circ}$ . At this temperature the viscosity of gelatin solutions made up as previously described, and not allowed to cool

<sup>4</sup> On the basis of Smith's work the question has been raised whether it would not be better to refer to a "transition region" with limits at  $15^{\circ}$  and  $38^{\circ}$  than to a "transition point" at  $38^{\circ}$ . The answer to this is not possible at the present time from the data at hand. Gelatin is made up of varying proportions of the different products of the hydrolysis of chondrin. Each of these different products of hydrolysis may have a different transition point. In such a case the product having the highest transition point will determine that of the entire sample.

On the other hand, the transition is extremely slow and requires days or weeks for completion at temperatures near the transition point. By reducing the temperature the "transition gradient" is increased and the change takes place more rapidly, reaching completion in a few hours at temperatures up to  $10^{\circ}$ . There is evidence substantiating each of these views. We are continuing the investigation along these two lines and at present are more inclined to the latter as being the true explanation.

below 40°, does not change with age. The gelation factor being eliminated it was thought a formula could be found which would apply.

The results for these solutions are given in Table III, and when plotted in Fig. 4 the logarithmic form of the graph suggested at once the application of Arrhenius' formula<sup>5</sup>

$$\log \frac{\eta}{\eta_0} = \theta c. \quad (1)$$

This formula, while first advanced for so called non-colloidal solutions has since been applied with success to protein solutions.<sup>6</sup> As first proposed

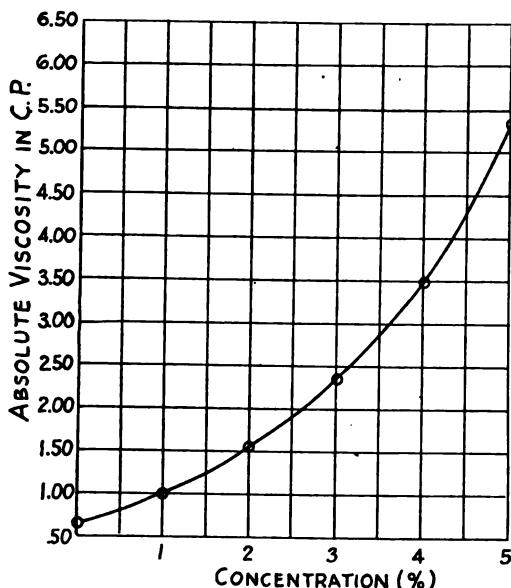


Fig. 4.—Variation of viscosity with concentration; solutions of at 3B gelatin 40°,  $P_H = 8.0$ .

by Arrhenius the concentration  $c$  could be expressed as volume, or weight per cent. Kendall<sup>7</sup> has modified this so that  $c$  is expressed as molecular concentration which modification has been accepted by Arrhenius as giving closer agreement with experimental data. Since the molecular weight of gelatin is unknown  $c$  has been expressed in weight concentration and the formula applied to these data. The average value for  $\theta$  when substituted in the original equation gives a calculated viscosity equal to the observed viscosity within the limits of accuracy of the latter,  $c$  being taken as per cent. concentration by weight.

<sup>5</sup> Arrhenius, *Z. physik. Chem.*, **1**, 285 (1887).

<sup>6</sup> Arrhenius, *Medd. K. Vetenskapsakad. Nobelinst.*, **3**, 13 (1916); *Biochem. J.*, **11**, 112 (1917).

<sup>7</sup> Kendall, *Medd. K. Vetenskapsakad. Nobelinst.*, **2**, 25 (1913).

TABLE III  
 VARIATION OF VISCOSITY WITH CONCENTRATION OF GELATIN SOLUTIONS AT 40° AND  
 P<sub>H</sub> 8.0

Concentration of gelatin %	Observed absolute viscosity C. p.	Calculated viscosity C. p.	$\eta$
0	0.656 <sup>a</sup>		
1	1.00	1.00	0.1831
2	1.55	1.53	0.1867
3	2.37	2.33	0.1858
4	3.47	3.55	0.1810
5	5.33	5.42	0.1818
Ave.			0.1836

Arrhenius<sup>b</sup> considers that for substances like proteins, whose molecules are extremely large compared with those of water,  $c$  may be expressed sufficiently accurately by the expression

$$c = \frac{100 p}{100 - (n + 1)p} \quad (2)$$

where  $p$  is the number of grams of solute in 100 g. of solution, and  $n$  is the hydration factor, i. e., the number of grams of solvent associated with each gram of solute and therefore withdrawn from solution. Substituting this value in (1) we have<sup>a</sup>

$$\log \frac{\eta}{\eta_0} = \Theta \frac{100 p}{100 - (n + 1)p} \quad (3)$$

$$\text{and } n + 1 = \frac{100}{p} - \frac{100}{\log \frac{\eta}{\eta_0}} \quad (4)$$

$$n + 1 = \frac{100}{p_1} - \frac{100 \Theta}{\log \frac{\eta_1}{\eta_0}} = \frac{100}{p_2} - \frac{100 \Theta}{\log \frac{\eta_2}{\eta_0}} \quad (5)$$

$$\Theta = \left( \frac{1}{p_1} - \frac{1}{p_2} \right) \div \left( \frac{1}{\log \frac{\eta_1}{\eta_0}} - \frac{1}{\log \frac{\eta_2}{\eta_0}} \right) \quad (6)$$

This gives us a method for solving for  $\Theta$  on the assumption that the gelatin is hydrated in solution at 40°. By combining the values for a 1% solution with each of the others and solving for  $\Theta$  in Equation 6 we obtain values for  $\Theta$  as follows: (1%-2%), 0.1796; (1%-3%), 0.1816; (1%-4%), 0.1838; (1%-5%), 0.1834; average,  $\Theta$  0.1821. Substituting this value in Equation 4 we obtain values for  $n$  as follows: 1%, -0.43; 2%, +0.23; 3%, -0.31; 4%, -1.18; 5%, -1.01. These values are well within the experimental error in determining viscosity and indicate that when gelatin is hydrated in solution at 40° the degree of hydration is very slight, cer-

<sup>a</sup> Bingham, *Bur. Standards, Bull.*, 298, 74 (1917).

<sup>b</sup> Hatschek, *Biochem. J.*, 10, 325 (1916).

tainly not greater than 1%. The agreement between the calculated and observed viscosities in Table III indicates the same fact because these values were calculated on the assumption that the gelatin is not hydrated.

Hatschek<sup>10</sup> has proposed the formula  $\frac{\eta_0}{\eta} = 1 - \sqrt[3]{\phi}$  where  $\eta$  as usual is

the viscosity of the solution,  $\eta_0$  that of the solvent and  $100 \phi$  is the volume per cent. of the dissolved substance with its associated solvent. Regarding this formula Smoluchowski<sup>11</sup> says: "It may be an interpolation formula of a certain use in many cases, but it is probably of no general significance, as it is impossible to give it a rational foundation." Hatschek<sup>9</sup>

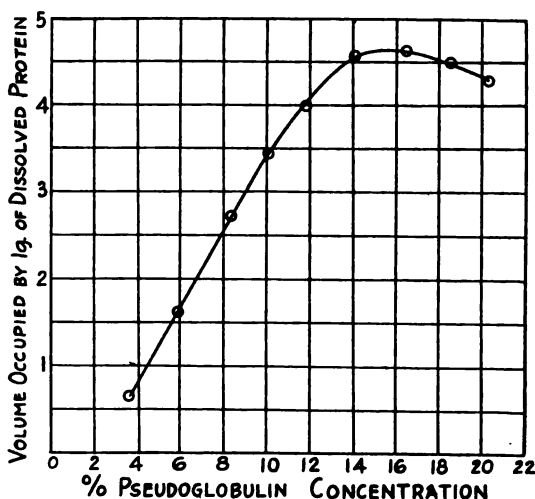


Fig. 5.—From Chick.

calls attention to the application of his formula by Miss Chick<sup>12</sup> to some of her results on various proteins and emphasizes the fact that where the dissolved substance with its associated solvent occupies more than 50% of the total volume the formula holds very well. Arrhenius<sup>6</sup> shows that Hatschek's equation does not give constant values for the degree of hydration even under the conditions imposed by Hatschek. Arrhenius also suggests that it is improbable that a continuous function such as the degree of hydration of these various proteins should be represented by an equation for a discontinuous function. In Fig. 5 we have plotted the values obtained by Miss Chick for pseudoglobulin. In selecting her values for the hydration constant she chose points at the top of the curve. This is the only point where Hatschek's formula can possibly

<sup>10</sup> Hatschek, *Kolloidchem.*, 8, 34 (1911); 11, 284 (1912); 12, 238 (1913).

<sup>11</sup> Smoluchowski, *Kolloid Z.*, 18, 190 (1916).

<sup>12</sup> Chick, *Biochem. J.*, 8, 261 (1914).

give anywhere near constant values. Generally the solutions become so viscous that few values can be determined on the descending portion of the concentration-volume curve.

A glance at Fig. 6 indicates why Hatschek's formula gives more nearly constant hydration values above 50% than below. Up to the point where  $\phi = 0.5$  or where the solute with its associated solvent equals 50% of the total volume the viscosity increases only to 4.858 times that of the solvent. As  $\phi$  increases from 0.5 to 1 the viscosity increases from 4.858 to infinity. In other words, over that portion of the curve up to  $\phi = 0.5$  the viscosity increases fairly uniformly with the total volume occupied by the solute with its associated solvent. Beyond the point

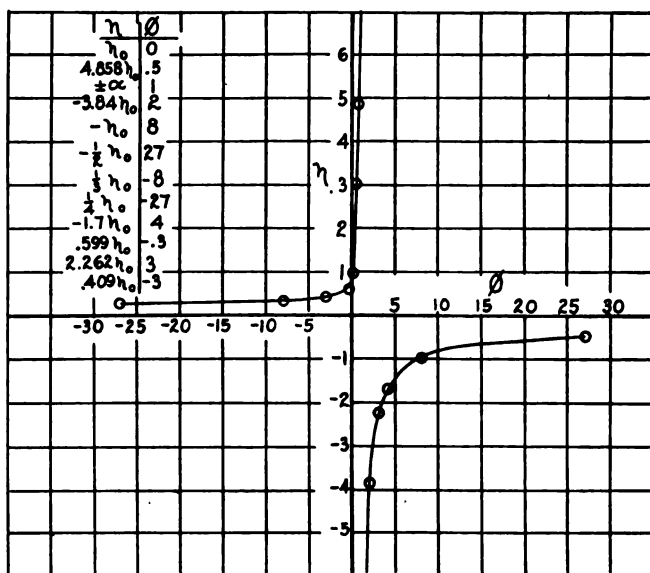


Fig. 6.—Graph of Hatschek's hydration formula  $\frac{\eta_0}{\eta} = 1 - \sqrt{\phi}$ , assuming  $\eta_0 = 1$ .

where  $\phi = 0.5$  the formula would have the viscosity increase out of all proportion to  $\phi$  if  $\phi$  continued to increase at a uniform rate. Now the experimentally determined viscosity does not increase as rapidly as is demanded by the formula so that  $\phi$  must change from an increasing to a decreasing function. That section of the curve where  $\phi$  is undergoing a change of direction will indicate a more constant value for the degree of hydration. Beyond this point the degree of hydration will decrease rapidly. Since most solutions are too viscous to manipulate on this downward part of the curve (Fig. 5) by selecting values above  $\phi = 0.5$  they necessarily come on this flat section.

When Hatschek's formula is applied to the results in Table III it gives

the following values for  $\phi$  and for the volume occupied by 1 g. of gelatin with its associated water.

TABLE IV

Concentration of gelatin. Weight per cent.	$\phi$	Volume occupied by 1 g. of gelatin plus associated water
1	0.0407	4.07
2	0.1917	9.58
3	0.3781	12.60
4	0.5333	13.33
5	0.6741	13.48

B does not even approach a constant value until  $\phi$  is greater than 0.5. We have just seen that from the nature of the equation this is exactly what is to be expected and the formula apparently has no general application. Instead of each gram of solute associating itself with an increasing amount of water with decreasing concentration of water (increasing concentration of solute) we would expect the reverse to be the case. Hatschek was at first enthusiastic over Miss Chick's results because they gave a constant hydration factor. He then proceeds to apply the formula to Para rubber-benzene solutions. A 0.5% solution of Para rubber in benzene gives an association factor of 62%. Obviously a 1% solution must give a lower factor. It seems certain then that Hatschek's formula when applied to these solutions gives no information as to their behavior, while Arrhenius' equation expresses the results within the experimental accuracy. Naturally Einstein's formula  $\eta = \eta_0 (1 + 2.5\phi)$  does not apply, for the viscosity is increasing more rapidly than the equation permits. As Smoluchowski<sup>11</sup> points out "For the sphere this value ( $k = 2.5$ ) has evidently a minimum value. There is no excuse for Hatschek's higher values.  $K$  decreases with increasing diameter of the spherical particles." Hess<sup>12</sup> under the title "Theory of the Viscosity of Heterogeneous Systems"

has proposed the formula  $\eta_s = \frac{\eta}{1 - aK}$  where  $\eta_s$  is the viscosity of the

suspension,  $\eta$  the viscosity of the fluid dispersion medium,  $K$  is the volume of the suspended particles and  $a$  is a characteristic constant for each substance and always greater than 1. The formula was tested with suspensions of blood corpuscles which offer the advantage of great uniformity. For cattle blood,  $a$  is 1.6-1.52; for pig blood, 1.42; for sheep blood, 1.52.

Before considering the application of this formula to the data under discussion let us consider its relation to Einstein's formula.

Hess' equation is

$$\eta = \frac{\eta_0}{1 - aK} \quad \text{or} \quad \frac{\eta}{\eta_0} = \frac{1}{1 - aK};$$

<sup>12</sup> Hess, *Kolloid Z.*, 27, 1 (1920).



Einstein's equation is

$$\eta = \eta_0(1 + 2.5\phi) \quad \text{or} \quad \frac{\eta}{\eta_0} = 1 + 2.5\phi;$$

whence

$$\frac{1}{1 - aK} = 1 + 2.5\phi.$$

and

$$1 + aK + a^2K^2 + a^3K^3 + \dots = 1 + 2.5\phi.$$

Einstein's  $2.5\phi$  represents the summation of  $aK + a^2K^2 + \dots$  and since neither holds except for dilute solutions  $aK = 2.5$  and the identity of the two equations is evident. Hatschek<sup>14</sup> proves the identity of Hess' formula and his own. It would seem then that Hatschek's formula as well as that of Hess is identical with Einstein's, although Hatschek does not even mention Einstein in his article.

### Variation of Viscosity with Temperature

The viscosity of 1% solutions of 3B gelatin of  $P_H$  8.0 was investigated over a temperature range of 25° to 60°. These results are plotted in Fig. 7 together with the viscosity of water over the same range. It will be seen from the figure that the viscosity is not a simple function of the temperature. At 40° and above, the viscosity of the solutions did not change with age. Above 65° Arisz<sup>15</sup> has shown that glycerine-water-gelatin solutions decrease in viscosity with aging of solution. The higher the temperature the more rapid the decrease. We have shown<sup>1</sup> that the same is true for water-gelatin solutions and that this decreasing viscosity is due to hydrolysis of the gelatin. Arisz suggested but did not prove this point. We also showed that hydrogen and hydroxyl ions catalyze this hydrolysis and established the concentrations of these ions necessary to hydrolyze gelatin solutions below the limit set by Arisz. Furthermore, even at 25° certain concentrations of hydrogen and hydroxyl ions caused a continued hydrolysis of gelatin. Northrup<sup>16</sup> has studied this question in minute detail over the entire range of hydrogen-ion concentration. He finds that the hydrolysis is 10 times as rapid at 65° as at 40°. Inasmuch as our measurements were made at  $P_H$  8.0, hydrolysis had too slight an effect to make itself felt in the results.

It will be seen from Fig. 7 that the viscosity is not a simple function of the temperature. Above 40° the viscosity of the solutions did not change with age. At 35° and below the viscosity increased with age. This increase in viscosity with aging of solution accounts for the curve

<sup>14</sup> Hatschek, *Kolloid Z.*, **27**, 163 (1920).

<sup>15</sup> Arisz, *Kolloidchem. Beihefte*, **7**, 1 (1915).

<sup>16</sup> Northrup, *J. Gen. Physiol.*, **3**, 6, 715 (1921).

being steeper below  $35^{\circ}$  than it is above  $40^{\circ}$ . Below  $35^{\circ}$  the gelation factor manifests itself while above  $40^{\circ}$  this factor is absent. By prolonging the curves at  $35^{\circ}$  and  $40^{\circ}$  as dotted lines they are found to cross at  $38^{\circ}$ . The transition point of gelatin should lie close to this point.

#### Variation of Viscosity with Hydrogen-ion Concentration at $40^{\circ}$

It has been pointed out in a previous article<sup>1</sup> that at  $25^{\circ}$  the forms of the hydrogen-ion concentration-viscosity curves will differ considerably,

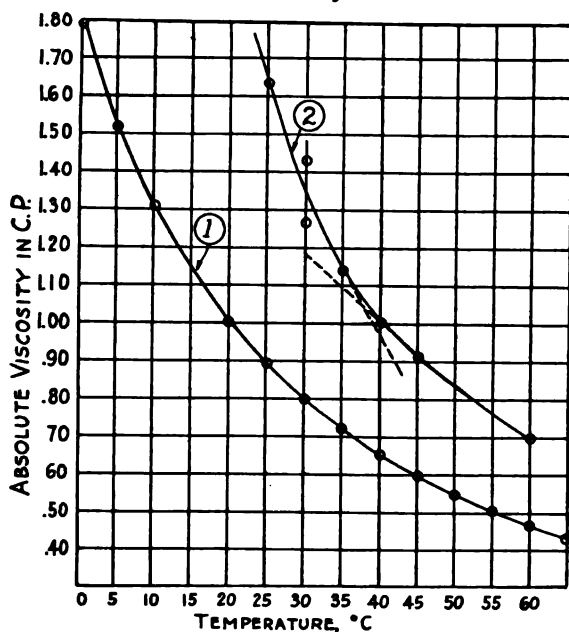


Fig. 7.—Variation of viscosity with temperature, 1 = water, 2 = 1% gelatin solution 3B,  $P_H = 8.0$ .

especially on the alkaline side of the iso-electric point, depending upon the age of solution at which the viscosity is determined. In that paper data were given showing that the form of the curve meant little unless the age of solution and the time rate of increase in viscosity were given. Since the viscosity of gelatin solutions does not increase with age at  $40^{\circ}$  it seemed desirable to determine the effect of different acidities at this temperature.

Accordingly, 1% solutions of 3B gelatin were investigated over a range of  $P_H$  values from 1.7 to 12.3. These results are plotted in Fig. 8 and show a very distinct maximum in the viscosity at  $P_H$  3.5. At  $P_H$  11.0 to 12.0 there is another maximum in the viscosity. Due to the very rapid hydrolysis of the gelatin at this temperature and at  $P_H$  values greater than 10 the viscosity decreased so rapidly with aging of solution that it was impossible to locate the exact point of maximum viscosity.

The interesting part of this curve lies not so much in the maxima which coincide very closely with those obtained by Loeb<sup>17</sup> as in the minimum point of viscosity which lies between  $P_H$  7 and  $P_H$  8. There can be no doubt whatever that this is the point of minimum viscosity at this temperature, for not only were the viscosities and  $P_H$  values checked very carefully, but the slope of the curve on both sides of the minimum agrees with this point. This may very well be the result of absence of the age effect on viscosity; the minimum obtained at  $P_H$  4.7 at  $25^\circ$  would then be an apparent minimum only.

Consider the action of the two major factors affecting gelatin solutions at  $25^\circ$  and in the  $P_H$  range 3.5–10.0. Addition of alkali causes

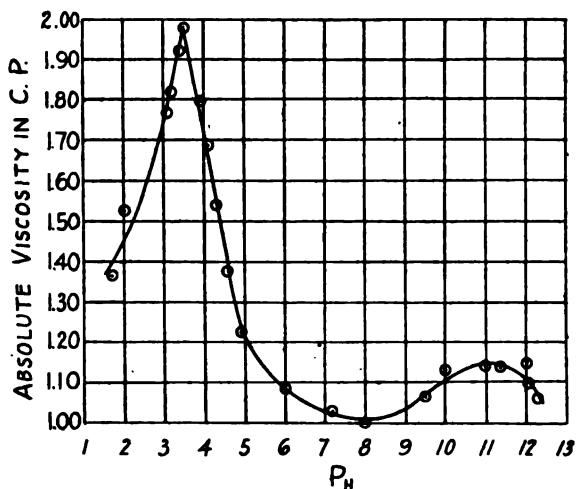


Fig. 8.—Variation of viscosity with  $P_H$ ; 1% solutions of 3B gelatin at  $40^\circ$ .

a decrease ( $R$ ) in viscosity at  $P_H$  3.5. At the same time there is an increase in the rate of gelation ( $g$ ) caused by the addition of alkali.<sup>1</sup> Where the algebraic sum of these factors  $g + R$  equals zero ( $R$  being negative at this point) there will be a maximum or a minimum. At  $40^\circ$  this gelation factor is absent; consequently we are getting the true effect of hydrogen-ion concentration on viscosity. It has been suggested that the ash content of this gelatin, which amounted to 0.5 per cent., influenced the point of minimum viscosity. That this is unlikely is seen from the fact that both Loeb and ourselves have repeatedly shown that when the hydrogen concentration remains the same the presence of nonprecipitating salts has no effect other than their effect on the water itself. There may be considerable difficulty in reconciling this minimum viscosity at  $P_H$  about 8.0 with the iso-electric point at  $P_H$  4.7.

<sup>17</sup> Loeb, *J. Gen. Physiol.*, 3, 85 (1920).

### Summary

1. The density in grams per cubic centimeter of a gelatin solution of any concentration at any temperature is equal to the density of water at that temperature plus 0.00290 multiplied by the percentage concentration of the gelatin by weight.

2. The viscosities of gelatin solutions of various concentrations at 40° conform to Arrhenius' viscosity formula.

3. The viscosity-temperature curve of gelatin shows a sharp deflection at the transition point of the gelatin.

4. There are two maxima in the viscosity-hydrogen-ion concentration curve for gelatin solutions at 40°. These maxima are about equidistant from the neutral point of water and the effect of the iso-electric point  $P_H$  4.7 is not noticeable on the curve.

5. The transition point of gelatin Sol form A  $\rightleftharpoons$  Gel form B is at a temperature of 38.03°.

6. A change has been suggested in the method of estimating age of solution for viscosity determinations at temperatures below the transition point of the gelatin

NEW YORK, N. Y.

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[CONTRIBUTION FROM THE RESEARCH LABORATORY OF PHYSICAL CHEMISTRY OF THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY, NO. 139]

## THE PRESSURE OF OXYGEN IN EQUILIBRIUM WITH SILVER OXIDE

BY FREDERICK G. KEYES AND H. HARA

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### Introduction

The transfer of oxygen from the chemically combined or bound condition to the free condition is somewhat analogous to the passage of a substance from the solid phase to the gaseous phase. The combined oxygen in an oxide (or the combined carbon dioxide in a carbonate) may be conceived as occupying at any temperature and pressure a definite partial specific volume and regarded as the specific volume of the compound less the specific volume of the metal or other atomic residue. Thus for silver oxide the volume of a gram of oxygen, in the combined condition, obtained from the densities of silver oxide ( $Ag_2O$ ) and silver, would be 0.6472 cc. at ordinary temperatures, which in fact in this instance is about the estimated volume of 1 g. of oxygen in the free solid condition at  $-273^\circ$ .

In the case of silver oxide large pressures of oxygen are obtained at comparatively low temperatures and the gas law  $pv = RT$  is insufficient as an equation to calculate the equilibrium volumes of the oxygen. G. N.

Lewis,<sup>1</sup> who first studied the equilibrium conditions of this oxide, applied to his measurements a method of thermodynamic correlation based on the use of the Clausius equation ( $Q = T \frac{dp}{dT} \Delta v$ ), and employed the equation  $v = \frac{RT}{p}$  which was sufficient for the range of pressures measured.

The term  $\Delta v$  represents the increase in volume of the products of the decomposition over the volume of the factors. For two mols of silver oxide  $\Delta v$  is the sum of the volumes of 1 mol of oxygen and 4 mols of silver diminished by the volume of 2 mols of silver oxide. The quantity amounts, therefore, to the difference in the volume of free oxygen diminished by the volume difference between silver oxide and free silver, all under the same equilibrium conditions of pressure and temperature. In support of the analogy of this type of equilibrium to that of a pure substance it may be pointed out that the volume of the free oxygen diminishes continuously with the rising pressure as does the saturation volume in the case of a pure liquid or solid. The volume difference between silver oxide and silver also increases regularly. The analogy will be really complete, however, if the heats of the transfer from combined to free state diminish and eventually vanish at the point where  $\Delta v$  is zero. It was a prime object of this work to examine as far as feasible this possibility. The density data available are incomplete for silver oxide, but the coefficients of expansion of the salts AgCl and AgBr are only about half again as large as that of silver, and if silver oxide is approximately similar the volume difference of salt and metal would increase very slowly with the temperature. Lacking data on the expansion of silver oxide the volume difference for silver oxide-silver will, in this paper, be taken as constant. The data to follow indicate that  $\Delta v$  may eventually vanish with rising temperature and pressure, but since  $Q$  finally increases with rising temperature  $\frac{dp}{dT} \Delta v$  may become indeterminate.

The volumes of the free oxygen can be easily calculated by means of the equation of state<sup>2</sup> for oxygen when the equilibrium pressures and temperatures of oxygen over silver oxide are given. The constants of the oxygen equation of state were obtained from Amagat's data extending over a temperature range of 200° and pressure range of 1000 atmospheres. The data in connection with the equilibrium in the present investigation extend to a pressure of only about 400 atmospheres, but sufficient data are available not only to establish this important equilibrium, but to

<sup>1</sup> Lewis, *Z. physik. Chem.*, **55**, 449 (1906). The equilibrium values presented in this paper were sent some months ago to Professor Lewis to be used in certain calculations in connection with his free energy studies.

<sup>2</sup> *Proc. Nat. Acad. Sci.*, **3**, 323 (1917); *THIS JOURNAL*, **43**, 1452 (1921).

indicate that  $\Delta v$  probably does not vanish below the melting point of silver or perhaps that of silver oxide.

### Apparatus Details

The material in which the silver oxide was contained was of sterling silver reinforced by a steel jacket represented in Fig. 1.

The interior of the steel member G of diameter 12 mm. was covered uniformly with a layer of silver solder and then filled with molten sterling silver rubbed into soldering contact with the walls of the steel member. The silver case of the latter was bored out to a diameter of about 8 mm. The steel sheath C was filled with silver in a manner similar to G, bored, and left with a silver end which filled a section of the silver lining H of G. A chemically pure silver ring F served as a closing gasket forced to a tight closure by means of the steel ring E driven by the nut D. The lead tube A was prepared by drawing down a steel tube which inclosed a silver tube, and the composite tube so formed was silver soldered as indicated at B.

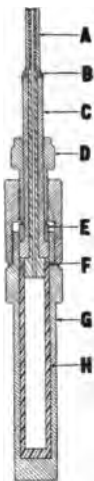


Fig. 1.

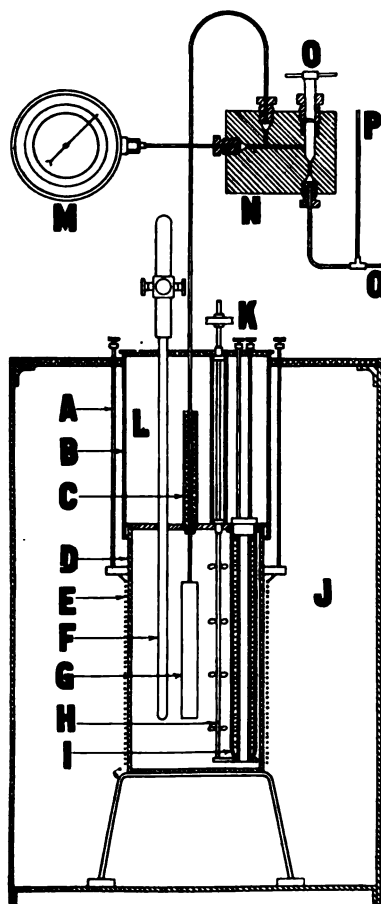


Fig. 2.

The constant temperature bath, Fig. 2, consisted of a sodium nitrate-potassium nitrate mixture contained in a steel vessel about which was wound a Nichrome resistance winding E. Two heats were provided by means of 3 terminal connections, one of which is designated by A. The tube G containing the material was passed through the steel cover of the bath which carried the stirrer and supplementary heater used for regulation. The space L was filled with insulating material, and the platinum resistance thermometer F served to measure the temperature. The connecting block N carried a stopcock O which served to close the bomb from a pump used to inject pure oxygen, since at the higher temperatures the volume of the apparatus was large enough to exhaust the oxygen contained in the quantity of silver oxide under observation. The oxygen pump was advantageous in changing at will the relative amounts of silver and silver oxide in the bomb and thus approaching the equilibrium pressure from higher and lower pressures.

Pressures were measured on the gage M indicating to 2 lbs. The gage was calibrated by means of one of the standard gages of the floating piston type in use in this Laboratory whose constant was obtained by direct comparison with a 9-meter column of mercury.

The silver oxide employed was prepared from c. p. silver nitrate solution obtained from c. p. silver. Crystals of  $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$  obtained by repeated crystallizations were used for the precipitating solution and the silver oxide was washed with distilled water free from carbon dioxide. Three days' washing was required to remove all traces of barium nitrate. The silver oxide was dried in a special bomb through which dry air, free from carbon dioxide, was circulated. The temperature of the drying was gradually raised to  $275^\circ$  during a period of 12 hours when the effluent gas from the bomb was found to be dry. The silver oxide gave on analysis a silver content of 93.09% as compared with 93.136% from the formula.

### Experimental Data

The measurements at temperatures lower than  $370^\circ$  confirm in every way the details given by Lewis regarding the slowness of the reaction at lower temperatures. In the present experiments about 20 hours was necessary to insure equilibrium at about  $300^\circ$  while above this temperature equilibrium was established very quickly. Altogether the pressures at 5 temperatures were measured, beginning at  $374^\circ$  and ending with  $500^\circ$ , and at each temperature 6 to 10 observations were made of the pressures as obtained from the formation and decomposition sides of the reaction. This control could be very conveniently obtained by means of the oxygen injection pump connected to the block N at P, Fig. 1. Oxygen could be allowed to escape through Q, which carried a steel stopcock not shown in the figure. Table I gives the new measurements and also the data of Lewis. The last column presents the pressures calculated for the measured temperatures by means of the equation written into the plot, Fig. 3. For comparison there has been drawn in this plot the dotted line representing the equation for the silver oxide equilibrium as computed by Pollitzer<sup>3</sup> on the basis of the Nernst theorem.

### Discussion of the Results

Fig. 3 and Table I present our data and those of Lewis in terms of the variables  $\log p$  and  $1/T$ . Within the limits of accuracy of the data it is evident that the points lie on a straight line whose equation is  $\log p = -\frac{2859}{T} + 6.2853$ . The free oxygen departs progressively from the simple gas laws, but the equation of state enables the volumes to be calculated at any temperature and pressure. The equation for  $\frac{dp}{dT}$  is obtained from the  $\log p$  equation given, or

$$\frac{dp}{dT} = \frac{2859 \times 2.3023}{T^2} p = \frac{6582}{T^2} p.$$

<sup>3</sup> "Die Berechnung Chemischer Affinitäten nach dem Nernstschen Wärmetheorem." Ferd. Enke, Stuttgart, 1912.

The heat of the reaction at any temperature is obtained from the Clausius equation by substituting therein the equation for  $\frac{dp}{dT}$ .

$$Q = 6582 \frac{p}{T} (v - 20.7)$$

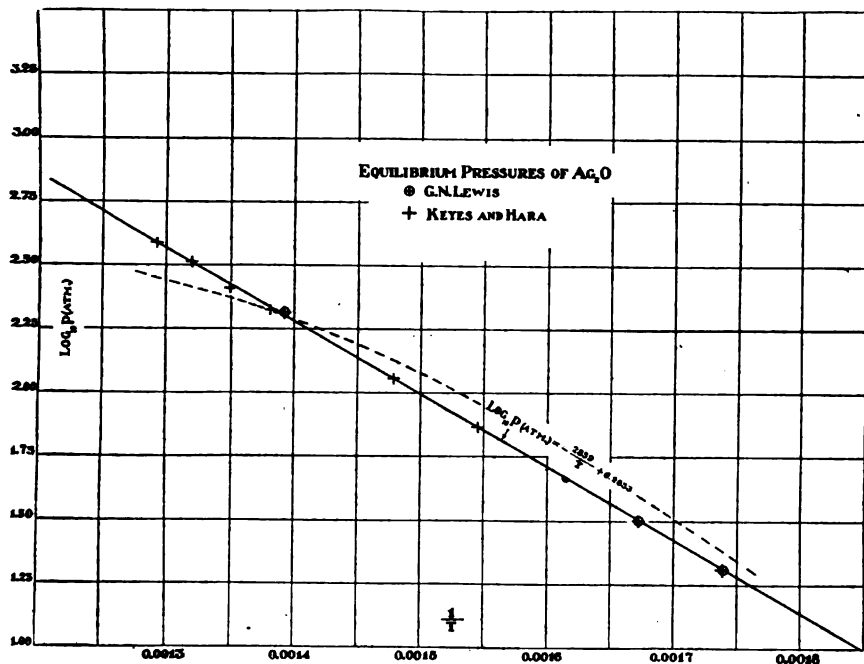


Fig. 3.

TABLE I  
EQUILIBRIUM PRESSURES IN ATMS. FOR THE REACTION  
 $2\text{Ag}_2\text{O} = 4\text{Ag} + \text{O}_2$

New Data

t	Pressure in Atm.			T, abs.	$\frac{1}{T} \times 10^3$	Log p Obs.	P calc. by equation.*
	To left	To right	Mean Observed				
374.0	.....	74.3	74.3	647.1	1.5454	1.8710	73.6
403.0	113	115.9	114.5	676.1	1.4791	2.0588	113.9
452.0	214.2	212.8	213.5	725.1	1.3791	2.3294	220.0
467.7	259.7	255.8	257.8	740.8	1.3499	2.4113	266.6
484.0	323.6	323.3	323.5	757.1	1.3208	2.5099	322.9
500.2	389.9	386.7	388.3	773.3	1.2932	2.5892	387.3
Equilibrium Pressures Measured by Lewis							
302.0	.....	.....	20.5	575.1	1.7388	1.3118	20.6
325.0	.....	.....	32.0	598.1	1.6720	1.5052	32.0
445.0	.....	.....	207.0	718.1	1.1393	1.3160	201.4

\* Equation for equilibrium pressure,  $\log p_{\text{atm}} = -\frac{2859}{T} + 6.2853$ .



where  $v$  is the volume of a mol of oxygen in the free state under equilibrium pressure  $p$  at the absolute temperature  $T$ . The number 20.7 is the volume difference between 2 mols of silver oxide and 4 mols of silver using the densities given for ordinary temperatures 7.5 and 10.5. Evidently this number should increase with the temperature, since the coefficient of expansion of silver oxide undoubtedly exceeds that of silver. The increase would be comparatively slight and will be neglected. It should be noted that the above simple equation involves no approximations, but is based on the complete Clausius equation and upon experiment.

In Table II will be found the pressures and volumes of oxygen at the equilibrium temperatures given in Col. 1. The volumes calculated by means of the perfect gas laws are also listed and it will be observed that a very fair approximation to the true volume is obtained up to about 20 atmospheres, while at about 4000 atmospheres the actual volume is somewhat more than twice the volume calculated by means of the perfect gas equation. At the corresponding temperature it will be noted also that  $\Delta v$  is 24.71 cc. A graph of  $\Delta v$  indicates that  $\Delta v$  might vanish in the neighborhood of  $1200^\circ$ , although this might occur at a lower temperature on account of the larger expansivity of silver oxide as compared with silver. The silver would melt below  $1200^\circ$  and possibly the oxide also which would introduce complexities due to solutions.

TABLE II  
PRESSURES AND VOLUMES OF OXYGEN

Equil. temp. °C.	Equil. press. Atms.	$\frac{dp}{dT}$	Volume <sup>a</sup> cc. per mol. by exact equat.	Volume cc. per mol. by perfect gas laws	$\Delta v$	Total heat cal. per mol. of O <sub>2</sub>	Internal heat, ( $Q - p\Delta v$ )
25							12640 <sup>b</sup>
200	1.75	0.05144	22208.0	22176.0	22187.3	13083	12142
300	19.8	0.397	2386.2	2374.4	2365.5	13042	11907
400	109.2	1.587	524.8	505.6	504.1	13046	11712
500	386.5	4.257	187.52	164.2	166.8	13313	11751
600	1028	8.856	95.81	69.76	75.1	14071	12204
700	2225	15.47	61.76	37.76	41.06	14973	12760
800	4179	23.90	45.41	21.12	24.70	15349	12848

<sup>a</sup> Equation of state for oxygen; pressure in atmospheres of 76 cm. of Hg; volume in cc. per g.

$$p = \frac{2.564}{v - \delta} T - \frac{1475}{(v + 0.09)^2}$$

$$\log \delta = 0.1420 - \frac{0.303}{v}$$

<sup>b</sup> Mean of Thomsen's and Berthelot's observed values combined with computations of Lewis, Ref. 1.

The last column gives the heat of the reaction diminished by the external work  $p \Delta v$  in calories. The specific heat of silver oxide has not been measured, but by Kopp's rule about 500 cal. would be added to the heat

at 200° giving 12642 cal. at ordinary temperatures, in excellent agreement with the mean of the observed values of Thomson and Berthelot and three others calculated by Lewis. It is of interest to observe that a minimum appears to exist at about 400–500° in the values of the internal heats, which indicates that the heat is tending to increasingly large values while  $\Delta v$  is diminishing continuously. The specific heat of silver oxide is required before further interpretation of the present equilibrium data is possible. The specific heats at low temperatures together with accurate values of the vapor pressure of liquid oxygen below one atmosphere will also provide material to test more adequately the application of the Nernst heat theorem to the type of equilibrium herein discussed.

### Summary

1. The equilibrium pressure of oxygen over silver and silver oxide has been measured, confirming the data of Lewis and extending them to higher pressures and temperatures.
2. The following equation (ordinarily derived by the use of the perfect gas law and by assuming the heat constant) is found empirically to represent the data exactly:

$$\log p = -2859/T + 6.2853,$$

where the pressure is in atmospheres, the temperature is degrees absolute, and common logarithms are used.

3. The Nernst heat-theorem equation, as given by Pollitzer to fit the data of Lewis, fails to represent the data.

4. Neglecting only the difference in the coefficient of expansion between silver oxide and silver, the following equation is derived from the Clausius equation for the external heat of the reaction, in calories per mol of oxygen,

$$Q = 6582 (v-20.7) p/T,$$

where  $v$  calculated from the equation of state for oxygen is given in cc. per mol.

5. The value for the internal heat at 25°, calculated with the aid of Kopp's rule, is 12642 cal., in agreement with the mean of the measurements and computations (12640 cal.) considered by Lewis.

6. The internal heats, though they pass through a minimum at about 400–500°, increase again with rising temperature.

7. The analogy between this chemical reaction and a simple evaporation, therefore, breaks down since no sign is shown of a critical point, with the heat equal to zero, although  $\Delta v$  appears to be diminishing progressively.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF STANFORD UNIVERSITY]

## THE AMMONO CARBONIC ACIDS

BY EDWARD C. FRANKLIN

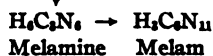
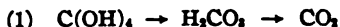
Received November 23, 1921

## Introduction

Ammono acids are compounds related to ammonia as the ordinary oxygen acids are related to water.<sup>1</sup> It follows therefore that the familiar substances guanidine, biguanide, cyanamide, dicyanodiamide and melamine as well as the less well known melam, melem, melon and hydromelonic acid, which many years ago were objects of intensive study,<sup>2</sup> are to be looked upon as ammono carbonic acids.

## Aquo Carbonic Acids and Ammono Carbonic Acids

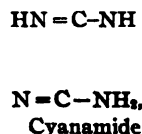
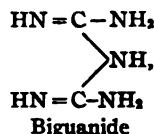
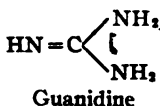
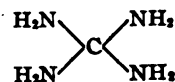
The formal analogy between the carbonic acids of the water or oxygen system on the one hand and the carbonic acids of the ammonia or nitrogen system on the other is shown by the following schemes which represent (1) aquo ortho carbonic acid and its dehydration products and (2) the compounds enumerated above represented as de-ammonation products of a purely hypothetical ammono ortho carbonic acid.<sup>3</sup>



<sup>1</sup> Cf. *Am. Chem. J.*, 47, 285 (1912); *Proc. Eighth Int. Cong. App. Chem.*, 6, 119 (1912).

<sup>2</sup> Liebig, *Ann.*, 10, 1 (1834); 50, 337 (1844); 53, 330 (1845); 95, 257 (1855). Laurent and Gerhardt, *Ann. chim. phys.*, [3] 19, 85 (1847).

<sup>3</sup> The following structural formulas are printed in the belief that the relations between the members of the group of compounds under consideration will thereby be made clearer. Those given for guanidine, biguanide, cyanamide, dicyanodiamide and melamine are the generally accepted formulas. The remaining compounds are represented as successive de-ammonation products of melamine which for this purpose is formulated as the amide of the trivalent nucleus,  $\text{C}_3\text{N}_3$ .



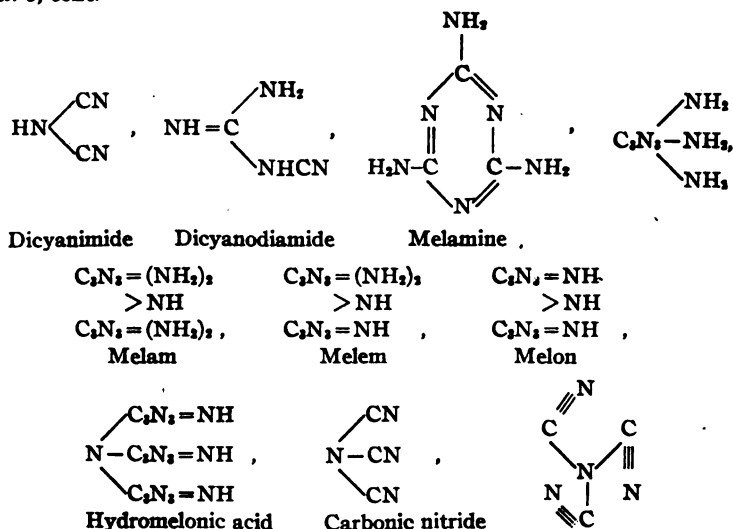
The first scheme, familiar for its frequent use to show the relations between ortho carbonic acid, ordinary carbonic acid and carbonic anhydride, calls for no comment other perhaps than to contrast the very limited number of compounds in this series of dehydration products with the much larger number of ammono carbonic acids listed in the second, and to note that the end product in the former is a gas, while all the compounds in the latter group are solids. Melon, the best known compound towards the end of the second scheme, is an insoluble, infusible substance which withstands without change a temperature approaching redness.

In the second scheme guanidine, biguanide, cyanamide and dicyanamide are represented as stepwise de-ammonation products of ammono ortho carbonic acid, dicyanodiamide and melamine as a dimer and a trimer, respectively, of cyanamide, while the remaining members of the group appear as successive de-ammonation products of melamine. For the most part the transformations indicated have been experimentally established.

*Guanidine to Melon.*—The action of water and ammonia, respectively, on chloropicrin or ethyl ortho carbonate might be expected to yield compounds of the respective formulas  $C(OH)_4$  and  $C(NH_2)_4$ . As a matter of fact, the products obtained are, in the first case, carbon dioxide, in the second, guanidine.<sup>4</sup> Guanidine thus appears as a de-ammonation product of an hypothetical ammono ortho carbonic acid just as carbon dioxide is usually assumed to be the dehydration product of the primarily formed ortho carbonic acid.

The second step in this process of de-ammonation, namely, the conver-

Ref. 3, cont.



Hofmann, *Ann.*, 139, 107 (1866); *Ber.*, 1, 145 (1868).

sion of guanidine into biguanide has been accomplished by carefully heating guanidine hydrochloride.<sup>5</sup>

Apparently neither guanidine nor biguanide has been converted into cyanamide by simple loss of ammonia. When guanidine carbonate,<sup>6</sup> or free guanidine<sup>7</sup> is heated melamine, a trimer of cyanamide, is obtained instead of cyanamide itself. However, the transformation of guanidine into cyanamide is easily accomplished by dissolving guanidine in fused sodium amide<sup>8</sup> or by heating it with quicklime.<sup>9</sup> It is safe to assume that biguanide may also be converted into cyanamide by the action of fused sodium amide.

In the table given above, cyanamide is represented either as losing ammonia to form dicyanimide or as undergoing polymerization to dicyandiamide. When cyanamide is heated it does not lose ammonia as might be expected to form dicyanimide. Instead, it undergoes polymerization first to dicyanodiamide<sup>10</sup> and thence to melamine.<sup>11</sup> The transformation of cyanamide into dicyanimide takes place when melon is dissolved in fused disodium cyanamide.<sup>12</sup>

At a higher temperature melamine loses ammonia to form melam which in turn is finally converted into melon. Further de-ammonation of melon to hydromelonic acid or to pure carbonic nitride has not been accomplished.

Returning to dicyanimide it is interesting to note that this substance on being heated is polymerized to melon instead of losing ammonia to form carbonic nitride.

*Melon to Guanidine.*—Among the inverse transformations but one case of simple addition of ammonia seems to be known. Rathke<sup>13</sup> found that melamine is formed when melem is heated with aqueous ammonia.

Cyanamide, in the form of its disodium salt, is formed when sodium melonate, sodium dicyanimide, melon, crude melam, melamine or dicyandiamide is dissolved in fused sodium amide. The ammonio carbonic acids,<sup>14</sup> hydromelonic acid, dicyanimide, melon and melam are thus ammonated, while melamine and dicyanodiamide are depolymerized to cyanamide, the only ammonio carbonic compound which is stable in the presence of an excess of the fused ammonio base.

The simple stepwise ammonation of cyanamide through biguanide to

<sup>5</sup> Bamberger and Dieckmann, *Ber.*, 25, 543 (1892).

<sup>6</sup> Nencke, *J. prakt. Chem.*, [2] 17, 235 (1878); Smolka and Friedreich, *Monatsh.*, 10, 91 (1889).

<sup>7</sup> Rathke, *Ber.*, 12, 778 (1879).

<sup>8</sup> Observations made in this laboratory.

<sup>9</sup> Emich, *Monatsh.*, 10, 334 (1889).

<sup>10</sup> Beilstein and Geuther, *Ann.*, 108, 99 (1858); 123, 241 (1862).

<sup>11</sup> Drechsel, *J. prakt. Chem.*, [2] 13, 331 (1876).

<sup>12</sup> See p. 497.

<sup>13</sup> Rathke, *Ber.*, 23, 1675 (1890).

<sup>14</sup> See p. 497.

guanidine has apparently never been realized. Cyanamide, however, is ammonated to guanidine when heated with ammonium chloride in alcoholic solution<sup>15</sup> and in a similar manner dicyandiamide is converted into biguanide.<sup>16</sup> Dicyanodiamide is also ammonated to biguanide when heated with ammoniacal cupric hydroxide solution.<sup>17</sup>

The final step in this ammonation series, namely, the formation of guanidine from biguanide has not been accomplished.

**Hydrolysis of the Ammono Carbonic Acids and the Ammonolysis of Aquo Carbonic Acid.**—In harmony with the view that compounds under consideration are ammono carbonic acids is the behavior of the ammono carbonic acids toward water, on the one hand, and the action of ammonia on aquo carbonic acid, or more generally, on the metallic carbonates, on the other. The ammono carbonic acids without exception when heated to a high temperature in the presence of water are hydrolyzed, usually through various mixed aquo ammono carbonic acids to carbon dioxide and ammonia in accordance with the general equation  $x\text{NH}_3 \cdot y\text{C}_3\text{N}_4 + 6y\text{H}_2\text{O} = 3y\text{CO}_2 + (x + 4y)\text{NH}_3$  in which  $x\text{NH}_3 \cdot y\text{C}_3\text{N}_4$  represents any one of the known ammono carbonic acids.<sup>18</sup>

The equation given above, read from right to left, represents the ammonolysis of aquo carbonic acid, or strictly speaking, carbonic anhydride, to an ammono carbonic acid. In experiments<sup>19</sup> in this direction, however, the ammonolysis has been carried only so far as the formation of urea, a mixed aquo ammono carbonic acid. The action of ammonia on ethyl ortho carbonate to form guanidine mentioned above and on calcium carbonate to form calcium cyanamide<sup>20</sup> are, in principle, reactions represented by the equation given above read from right to left.

**The Acid Properties of Guanidine and its De-ammonation Products.**—Among the members of the group of compounds under consideration it happens that only dicyanimide and hydromelonic acid are endowed with distinct acid properties. Cyanamide and dicyanodiamide are neutral in reaction. The first forms an unstable hydrochloride; both form metallic derivatives which, excepting certain highly insoluble salts of heavy metals, are practically completely hydrolyzed in the presence of water. Guanidine and biguanide show not the slightest acid properties in water solution. On the contrary, they behave as strong bases.<sup>21</sup> Mel-

<sup>15</sup> Erlenmeyer, *Ann.*, 146, 259 (1868); Bannow, *Ber.*, 4, 162 (1871).

<sup>16</sup> Smolka and Friedreich, *Monatsh.*, 9, 288 (1888); 10, 87 (1889); Ref. 5, p. 545.

<sup>17</sup> Herth, *ibid.*, 1, 94 (1880).

<sup>18</sup> For example, according to Knapp [*Ann.*, 21, 256 (1837)] melamine is hydrolyzed first to ammeline, thence to ammelide and finally to cyanuric acid.

<sup>19</sup> Mixter, *Am. Chem. J.*, 4, 35 (1882). Bourgeois, *Bull. soc. chim.*, [3] 7, 48 (1892); [3] 17, 474 (1897).

<sup>20</sup> Ger. pat. 138,456; *Zentr.*, 1903, I, 677.

<sup>21</sup> They are bases in the sense that ammonia is a base.

amine is a weak base. Melam, melem and melon are insoluble substances, concerning the acid properties of which practically nothing is known.

**Conclusion.**—The formal analogy existing between the two carbonic acids as derivatives of water on the one hand and the group of compounds under consideration, looked upon as derivatives of ammonia, on the other; the readiness with which one may pass stepwise from guanidine to melon by processes of de-ammonation and polymerization and, beginning with melon, return to guanidine by reactions of ammonation and depolymerization, the fact that each of these compounds may be hydrolyzed into carbon dioxide and ammonia are considerations which certainly lend support to the view that guanidine and its de-ammonation products are carbonic acids of the ammonia system.

This view is established, as it would seem, by the experimental work described below which shows that all the soluble members of this group of compounds are capable of forming metallic salts when liquid ammonia<sup>22</sup> instead of water is used as solvent in which to carry out the necessary reactions.

### Guanidine



Without going into details it will serve present purposes to point out that the large majority of methods listed in Beilstein's "Handbuch" for the preparation of guanidine involve processes of ammonolysis, ammonation or de-ammonation, while none is in disagreement with the view that it is an ammono carbonic acid.

The acid properties of guanidine are demonstrated by the following described reactions which have been carried out in liquid ammonia solutions.<sup>23</sup>

**Dipotassium Guanidine,  $\text{K}_2\text{H}_2\text{CN}_2$ .**—It has been found that potassium amide in excess added to a solution of guanidine nitrate<sup>24</sup> results in the formation of dipotassium guanidine which is insoluble and potassium ni-

<sup>22</sup> Compounds which, dissolved in ionizing solvents give a very low hydrogen-ion concentration, are not recognizable as acids in water solution because of the relatively high degree of ionization of water itself into hydrogen and hydroxyl ions. In liquid ammonia the very much lower degree of auto-ionization, which characterizes this solvent as compared with water, permits the acid properties of compounds which as acids are much too weak to be recognized as such in aqueous solutions to show themselves.

<sup>23</sup> For descriptions of methods of manipulating liquid ammonia solutions, cf. *THIS JOURNAL*, 27, 831 (1905); 29, 1694 (1907); 35, 1460 (1913); *J. Phys. Chem.*, 15, 915 (1911); 16, 694 (1912).

<sup>24</sup> It is a matter of very considerable difficulty to prepare pure guanidine, and once obtained it is so very hygroscopic that the exclusion of water and carbon dioxide from its liquid ammonia solution would be a tedious undertaking. It was therefore decided to make use of guanidine nitrate which is easily obtained in a pure dry state. This compound dissolved in liquid ammonia may be looked upon as a solution containing a mixture of nitric acid and guanidine.

trate which is soluble. The reaction is represented by the equation,  $\text{H}_5\text{CN}_3 \cdot \text{HNO}_3 + 3\text{KNH}_2 = \text{K}_2\text{H}_3\text{CN}_5 + \text{KNO}_3 + 3\text{NH}_3$ . The salt was obtained in the form of a non-crystalline powder which was vigorously hydrolyzed by the action of water into guanidine and potassium hydroxide.

**Preparation I.**—Half a gram of guanidine nitrate in solution in liquid ammonia added to a solution of 3 equivalents of potassium amide gave a bulky, amorphous precipitate which after standing for some time became denser and then settled fairly well. After the manner described in an earlier paper the precipitate was washed, dried in a vacuum and weighed. Preparatory to analysis the salt was treated first with water. Hydrochloric acid was then added which gave an aqueous solution of guanidine hydrochloride and potassium chloride. The specimen dried in a vacuum at  $20^\circ$  weighed 0.5397 g. One half gave 0.3333 g. of potassium sulfate. An accident prevented the determination of nitrogen. 0.50 g. of guanidine nitrate and 0.48 g. of potassium gave 0.54 g. of dipotassium guanidine and 0.42 g. of potassium nitrate. Calc. for  $\text{K}_2\text{H}_3\text{CN}_5$ , 0.55 g.; for  $\text{KNO}_3$ , 0.41 g.

**Preparation II.**—With the possibility in mind of obtaining a monopotassium salt a solution containing 2 equivalents of potassium amide was added to a solution of 0.30 g. of guanidine nitrate. No precipitate was formed. On concentrating the solution a crop of mixed crystals of potassium nitrate and, presumably, the monopotassium salt of guanidine separated from the solution. The isolation of the monopotassium salt from the mixture appearing impracticable, the reaction tube was opened and somewhat more than 4 additional equivalents of metallic potassium were introduced with the object in view of determining whether a salt could be obtained containing more than two atoms of potassium in the molecule. The solution of potassium amide formed by the action of ammonia on the potassium (in the presence of platinum black) was then added to the solution of the monopotassium salt with the result that a white amorphous precipitate was formed. The precipitate was washed and prepared for analysis in the usual way. The preparation dried in a vacuum at  $20^\circ$  weighed 0.3538 g. One half gave 0.2155 g. of  $\text{K}_2\text{SO}_4$ ; the other half gave 0.0580 g. of N.

It is to be noted that in the presence of a large excess of potassium amide only two of the acid hydrogen atoms were replaced.

**Preparation III.**—In a third experiment the potassium amide from 0.38 g. of potassium, and 0.30 g. of guanidine nitrate were used. The preparation dried in a vacuum at  $20^\circ$  weighed 0.3250 g. One half gave 0.2082 g. of  $\text{K}_2\text{SO}_4$ .

**Analysis.** Calc. for  $\text{K}_2\text{H}_3\text{CN}_5$ : K, 57.7; N, 31.0. Found: K, (I) 55.3, (II) 54.7, (III) 57.5; N, (II) 32.8.

**Monosilver Guanidine,  $\text{AgH}_4\text{CN}_3$ .**—This salt was obtained by the action of guanidine nitrate on silver amide in accordance with the equation  $\text{H}_5\text{CN}_3 \cdot \text{HNO}_3 + 2\text{AgNH}_2 = \text{AgH}_4\text{CN}_3 + \text{AgNO}_3 + 2\text{NH}_3$ . The salt is insoluble in liquid ammonia. It was not obtained in crystalline form.

**Preparation I.**—The silver amide obtained from 0.50 g. of silver nitrate was transferred in suspension to a solution containing 0.179 g. of guanidine nitrate, a quantity slightly in excess of the amount required for the formation of a monosilver salt. The first portions of the silver amide dissolved in the guanidine nitrate solution,\* the later portions failed to dissolve, nor could any marked change in the appearance of the insoluble residue be observed. The mixture was allowed to stand for 36 hours with occasional shaking with the object in view of transforming the insoluble silver amide

\* The solution of the first portions of the silver amide is the result of the action of nitric acid on silver amide to form silver nitrate which is soluble.



as completely as possible into the guanidine salt. Digestion was followed by a thorough washing of the precipitate. From the washings 0.245 g. of silver nitrate was recovered (calc. 0.250). The salt dried at 20° in a vacuum, was prepared for analysis by treatment, first with water, then with dil. sulfuric acid. The specimen weighed 0.3106 g. One half gave 0.1334 g. of AgCl. The other half gave 0.0322 g. of N. Calc. for  $\text{AgH}_2\text{CN}_3$ : Ag, 65.1; N, 25.4. Found: Ag, 64.8; N, 20.7. The low result for nitrogen is probably due to incomplete recovery of nitrogen by the Kjeldahl process.

### Triphenylguanidine

Accepting guanidine as an ammono carbonic acid, then the readily accessible triphenylguanidine is an ammono ester; and since the ammono-ester contains amide hydrogen it is an acid ester and should react with metallic amides to form salts. Moreover, in view of the fact that typically organic compounds are in a general way readily soluble in liquid ammonia, it was anticipated that the alkali metal salts of triphenylguanidine would be found to be sufficiently soluble to permit their crystallization from liquid ammonia.

**Dipotassium Triphenylguanidine,  $\text{K}_2(\text{C}_6\text{H}_5)_3\text{CN}_3$ .**—A well crystallized specimen of this salt has been prepared by the action of potassium amide on triphenylguanidine in accordance with the equation,  $\text{H}_2(\text{C}_6\text{H}_5)_3\text{CN}_3 + 2\text{KNH}_2 = \text{K}_2(\text{C}_6\text{H}_5)_3\text{CN}_3 + 2\text{NH}_3$ .

**Preparation I.**—One g. of triphenylguanidine in solution in liquid ammonia was added to a solution of potassium amide prepared from 0.50 g. of metallic potassium. After a short time and without concentrating the solution beautiful crystals began to separate on the walls and bottom of the tube. Without recrystallization the crop of crystals was washed several times with small quantities of the solvent and then dried in a vacuum at laboratory temperature. After drying the product took on the appearance of a salt which has undergone efflorescence. The salt therefore probably separates from solution with ammonia of crystallization. For analysis the salt was first hydrolyzed by the introduction of a small quantity of water, then dissolved in dilute alcohol and hydrochloric acid. The weight of the specimen was 0.2814 g. One half gave 0.0667 g. of  $\text{K}_2\text{SO}_4$ . The other half gave 0.0169 g. of N.

**Preparation II.**—The above described experiment was repeated, excepting that 1.00 g. of triphenylguanidine and the potassium amide from 0.31 g. of metallic potassium (2.2 equivalents of potassium amide per molecule of triphenylguanidine) were used and the product obtained was recrystallized. The light yellow, effloresced, crystals, when dried in a vacuum finally to 100°, weighed 0.9226 g. One half gave 0.2149 g. of  $\text{K}_2\text{SO}_4$ . The other half gave 0.0555 g. of N. Calc. for  $(\text{C}_6\text{H}_5)_3\text{K}_2\text{CN}_3$ : K, 21.5 N, 11.6. Found: K, (I) 21.3, (II) 21.0; N (I) 12.0, (II) 12.0.

A third preparation was undertaken with the object in view of determining the ammonia of crystallization. An unfortunate breakage in the apparatus put an end to the experiment, which was not repeated.

**Monopotassium Triphenylguanidine.**—One g. of triphenylguanidine and one equivalent of potassium amide were brought together in liquid ammonia solution. After the expenditure of much time in fruitless attempts to crystallize the salt a crop of extremely soluble crystals was finally obtained which was unfortunately lost while being prepared for analysis. There is little doubt of the existence of a monopotassium salt.

In view, however, of the time-consuming operations involved it did not seem worth while to repeat the experiment.

**Disodium Triphenylguanidine**,  $\text{Na}_2(\text{C}_6\text{H}_5)_3\text{CN}_3$  and  $\text{Na}_2(\text{C}_6\text{H}_5)_3\text{CN}_3 \cdot 3\text{NH}_3$ .—Sodium amide, which is but slightly soluble in liquid ammonia, dissolves readily in a solution of triphenylguanidine. The disodium salt separates well crystallized from very concentrated cold solutions. The disodium salt has also been prepared by the action of metallic sodium on the acid ester in accordance with the equation  $\text{H}_2(\text{C}_6\text{H}_5)_3\text{CN}_3 + 2\text{Na} = \text{Na}_2(\text{C}_6\text{H}_5)_3\text{CN}_3 + \text{H}_2$ .

**Preparation I.**—A solution containing 1.00 g. of triphenylguanidine was poured upon about 1.2 equivalents of sodium amide. The ammono base dissolved readily in the acid, forming a solution which on concentration at laboratory temperature, and even at  $-33^\circ$ , is converted into a viscous mass. When, however, the highly concentrated solution was cooled to a temperature near the freezing point of the solvent a crop of very soluble crystals was obtained. The mother liquor, in small quantity, was drained from the crystal mass, and the latter was then recrystallized from a small quantity of solvent. The preparation, dried at  $-33^\circ$ , and blackened as a result of the inadvertent entrance into the tube of a small quantity of air, weighed 0.3300 g. One half gave 0.0612 g. of  $\text{Na}_2\text{SO}_4$ . The other half gave 0.0298 g. of N. Losses of nitrogen were known to have occurred. Calc. for  $\text{Na}_2(\text{C}_6\text{H}_5)_3\text{CN}_3 \cdot 3\text{NH}_3$ : Na, 12.0; N, 22.0. Found: Na, 12.0; N, 18.0.

**Preparation II.**—To a solution containing 1.00 g. of triphenylguanidine portions of a solution containing 0.24 g. (3 equivalents) of metallic sodium were successively added. The blue color of the sodium solution was rapidly discharged as a result of the action of the acid on the metal. After the addition of approximately  $\frac{2}{3}$  of of the metal solution the disappearance of the color of further small portions became very slow. The hydrogen was not collected and measured. The resulting salt solution was evaporated to high concentration and cooled to  $-78^\circ$  when a crop of crystals separated. The product was drained of mother liquor, dissolved in pure solvent and recrystallized. The specimen was dried at  $-33^\circ$  in a vacuum. Then, maintaining a low pressure within the tube to prevent the melting of the salt in its ammonia of crystallization, the temperature was gradually raised to  $70^\circ$ , the ammonia given off, collected and determined. The amount was 0.0840 g. When dried the specimen weighed 0.5265 g. One half gave 0.1181 g. of  $\text{Na}_2\text{SO}_4$ . The other half gave 0.0333 g. of N. Calc. for  $\text{Na}_2(\text{C}_6\text{H}_5)_3\text{CN}_3$ : Na, 13.9; N, 12.7. Found: Na, 14.5; N, 12.7. Calc. for  $\text{Na}_2(\text{C}_6\text{H}_5)_3\text{CN}_3 \cdot 3\text{NH}_3$ : Na, 13.4. Found: 13.9.

**Monosilver Triphenylguanidine**,  $\text{HAg}(\text{C}_6\text{H}_5)_3\text{CN}_3$  and  $\text{HAg}(\text{C}_6\text{H}_5)_3\text{CN}_3 \cdot \text{NH}_3$ .—A monosilver salt of triphenylguanidine has been obtained by the action of a solution of the acid ester on silver amide as represented by the equation,  $\text{H}_2(\text{C}_6\text{H}_5)_3\text{CN}_3 + \text{AgNH}_2 = \text{HAg}(\text{C}_6\text{H}_5)_3\text{CN}_3 + \text{NH}_3$ . The salt separates from solution with one molecule of ammonia of crystallization which is lost in a vacuum at  $20^\circ$ .

**Preparation I.**—To 1.00 g. of silver nitrate in solution in liquid ammonia potassium amide prepared from 0.23 g. of metallic potassium was gradually added. The pure white precipitate of silver amide was thoroughly washed and then treated with a solution containing 1.13 g.<sup>28</sup> of triphenylguanidine. A considerable quantity of the silver

<sup>28</sup> It had been intended to use equimolecular quantities which would have required 1.69 g. of triphenylguanidine. The smaller quantity was used inadvertently.

amide dissolved but the solution becoming supersaturated, crystals of the salt began to separate before all the silver amide had gone into solution. The saturated solution was poured into the second leg of the reaction tube and evaporated to small volume. Crystals of the salt were deposited. The solvent distilled into the first leg of the tube was shaken up with the crude salt, the undissolved portion allowed to settle, after which the supernatant solution was poured into the second leg and evaporated to small volume. Additional pure salt was thus transferred to the second leg. This operation, once more repeated, gave an adequate specimen for analysis. The dried salt was treated first with water and then dissolved in a dilute alcohol sulfuric acid mixture preparatory to analysis. Dried in a vacuum at 20°, the preparation weighed 0.5373 g. One half gave 0.1101 g. of AgCl. The other half gave 0.0290 g. of N.

**Preparation II.**—In this experiment the silver amide prepared from 0.50 g. of silver nitrate was dissolved in a solution of 0.90 g. of triphenylguanidine or about 106% of the equivalent quantity. Soon after the amide had dissolved, beautiful crystals began forming on the walls and bottom of the reaction tube. The preparation was not recrystallized but was simply washed several times with pure solvent. The salt was then dried in a vacuum at -33°. On warming to laboratory temperature it lost 0.0231 g. of ammonia. Dried at 20° the specimen weighed 0.5565 g. One half gave 0.1069 g. of AgCl. The other half gave 0.0302 g. of N.

**Preparation III.**—0.50 g. of silver nitrate and 0.90 g. of triphenylguanidine were brought together in liquid ammonia solution in order to determine whether a silver salt might be formed in accordance with the equation  $\text{AgNO}_3 + \text{C}_6\text{H}_5\text{NC}(\text{NHC}_6\text{H}_5)_2 = \text{C}_6\text{H}_5\text{NC}(\text{NHC}_6\text{H}_5)(\text{NAgC}_6\text{H}_5) + \text{HNO}_3$ . The failure to obtain a crop of crystals from this solution was interpreted as showing that the silver salt of triphenylguanidine is soluble in a liquid ammonia solution of nitric acid. Neutralization of the acid (ammonium nitrate) by addition of potassium amide was followed by the immediate deposition of a crop of crystals. The crystals were washed and dried as described above for analysis. The salt was dried first at -33°. Heated at 70° in a vacuum it weighed 0.5529 g. It lost 0.0316 g. of ammonia between -33° and 70°. One half of the specimen gave 0.1134 g. of AgCl. The other half gave 0.0292 g. of N. The filtrate from AgCl gave 0.0298 g. of N. Calc. for  $\text{HAg}(\text{C}_6\text{H}_5)_2\text{CN}_3$ : Ag, 27.6; N, 10.7. Found: Ag, (I) 30.9, (II) 28.9, (III) 30.9; N, (I) 10.8, (II) 10.8, (III) 10.6. Calc. for  $\text{HAg}(\text{C}_6\text{H}_5)_2\text{CN}_3 \cdot \text{NH}_3$ : NH<sub>3</sub>, 4.1. Found: NH<sub>3</sub>, (II) 4.0, (III) 5.4. The high silver content in these preparations is probably due to the presence of disilver salt.

**Cuprous Triphenylguanidine,  $\text{HCu}(\text{C}_6\text{H}_5)_2\text{CN}_3$ .**—Monocuprous triphenylguanidine is formed as a brown insoluble powder without ammonia of crystallization by the action of a solution of the acid ester on cuprous amide. The pure salt is undoubtedly colorless.

**Preparation I.**—A portion of cuprous amide precipitated from a solution containing 1.00 g. of  $\text{Cu}(\text{NO}_3)_2 \cdot 4\text{NH}_3$ <sup>27</sup> was treated with a solution containing 1.13 g. of triphenylguanidine. The amide was not dissolved and there was no evidence of any action excepting some change in the appearance of the precipitate. The cuprous amide was left in contact with the solution overnight after which it was thoroughly washed in the usual manner. After drying in a vacuum at 20° the specimen weighing 0.7885 g. was dissolved in alcohol hydrochloric acid mixture for analysis. One half taken for the determination of nitrogen was lost. One fourth gave 0.0493 g. of CuO. Another fourth gave 0.0246 g. of N. A second portion of the salt which had stood longer in

<sup>27</sup> The action of potassium amide on a solution of cupric nitrate gives cuprous amide; cf. *THIS JOURNAL*, 29, 657 (1907); 43, 1501 (1921).

contact with the solution gave 19.9% of Cu. Calc. for  $\text{HCu}(\text{C}_2\text{H}_5)_3\text{CN}_3$ : Cu, 18.2; N, 12.0. Found: Cu, 20.0; N, 12.4.

The high copper content may very well be due to the presence of copper amide which escaped conversion into the salt.

### . Biguanide



Attempts have not yet been made to prepare biguanide salts using liquid ammonia as a solvent principally because of the prospective difficulties in the way of preparing a pure, dry specimen of the acid. It is practically certain that salts may be so prepared. The existence of a copper compound of the formula  $(\text{C}_2\text{H}_5\text{N}_3)_2\text{Cu} \cdot 2\text{H}_2\text{O}$  is recorded in the literature.

### Cyanamide



The acid properties of cyanamide are so well established—first by the recorded existence of a considerable number of metallic salts;<sup>28</sup> second, by the work of Franklin and Stafford<sup>29</sup> in preparing beautifully crystallized specimens of the magnesium salt by the action of a liquid ammonia solution of cyanamide on metallic magnesium; and third, by the observation of Franklin and Kraus<sup>30</sup> to the effect that liquid ammonia solutions of cyanamide are fair conductors of electricity—that it was not considered necessary to the present purpose to prepare further salts in liquid ammonia solution by the action of cyanamide on ammono bases. It may be assumed as a matter of course that salts may be so made.

Every one of the numerous methods collected in Beilstein for the formation of cyanamide and its salts is in harmony with the view that cyanamide is a carbonic acid of the ammonia system. Since however a detailed discussion of all the reactions involved would lead too far, a limited number which show clearly and simply the strict analogy between cyanamide and its salts on the one hand and carbonic acid and the metallic carbonates on the other will be briefly considered.

The best known reaction for the formation of a salt of cyanamide is that involved in the commercial preparation of calcium cyanamide. When calcium carbide is heated in the presence of nitrogen nitridation takes place with the result that calcium cyanamide is formed in accordance with the equation,  $\text{CaC}_2 + \text{N}_2 = \text{CaCN}_2 + \text{C}$ , just as similar treatment with oxygen converts calcium carbide into aquo carbonate of calcium as represented by the equation  $\text{CaC}_2 + 5\text{O} = \text{CaCO}_3 + \text{CO}_2$ . The analogy between the two processes is obvious.

Of considerable importance in its bearing on the view that cyanamide

<sup>28</sup> Beilstein, "Handbuch der organischen Chemie.," Deutsche Chemische Gesellschaft, 4th Ed., III, 28 (1921).

<sup>29</sup> Franklin and Stafford, *Am. Chem. J.*, 28, 105 (1902).

<sup>30</sup> Franklin and Kraus, *THIS JOURNAL*, 27, 195 (1905).

is an ammonio acid is the reaction represented by the equation,  $\text{CaCN}_2 + 3\text{H}_2\text{O} = \text{CaCO}_3 + 2\text{NH}_3$ , whereby ammonia is obtained from calcium cyanamide. This equation represents a well-known type of reaction, namely, the hydrolysis of an ammonio acid to an aquo acid. For example, the mixed aquo ammonio acetic acid, acetamide, is easily hydrolyzed to aquo acetic acid and ammonia as represented by the equation,  $\text{CH}_3\text{-CONH}_2 + \text{H}_2\text{O} = \text{CH}_3\text{COOH} + \text{NH}_3$ . Moreover, just as aquo acetic acid may be ammonolyzed to aquo ammonio acetic acid and water as represented by the above equation read from right to left, so also has the ammonolysis of aquo carbonate of calcium to the ammonio carbonate been accomplished as represented by the second equation above read from right to left,<sup>31</sup> in accordance with the specifications of a German patent.

In the abstract of this patent it is stated that barium and lead carbonates have in this manner been converted into the respective cyanamide salts. These results have been confirmed in this laboratory and it has also been found that cyanamide salts of calcium, sodium, potassium and lithium are formed when the carbonates of these metals are heated in a platinum crucible in an atmosphere of ammonia. The formation of cyanamide in each experiment was shown by dissolving the melt in water, adding aqua ammonia and obtaining the characteristic yellow precipitate of disilver cyanamide by the addition of ammoniacal silver nitrate.

This formation of cyanamide by the action of ammonia on the alkali carbonates has apparently never been observed before but such formation was certainly to be expected in view of recorded facts. Siepermann<sup>32</sup> found that ammonia acts on hot potassium carbonate in accordance with the equation  $\text{K}_2\text{CO}_3 + \text{NH}_3 = \text{KCNO} + \text{KOH} + \text{H}_2\text{O}$ . Since Drechsel<sup>33</sup> observed the formation of alkali cyanamide on fusing a mixture of potassium cyanate and sodium hydroxide as represented by the equation  $2\text{KNCO} + 2\text{KOH} = \text{K}_2\text{CN}_2 + \text{K}_2\text{CO}_3^{33a} + \text{H}_2\text{O}$ , it necessarily follows that Siepermann's reaction mixture must have contained cyanamide.

Siepermann's equation represents the ammonolysis of an aquo carbonate to an aquo ammonio carbonate; Drechsel's represents the conversion of a mixed aquo ammonio carbonate into a mixture of an aquo carbonate and an ammonio carbonate.

Drechsel<sup>34</sup> found that calcium cyanate, when heated, decomposes

<sup>31</sup> Ger. pat. 139,456; *Zentr.*, 1903, I, 577.

<sup>32</sup> Siepermann, Ger. pat. 38,012; *Ber.*, 20, Ref., 180 (1887).

<sup>33</sup> Drechsel, *J. prakt. Chem.*, [2] 21, 89 (1880).

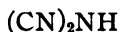
<sup>33a</sup> This reaction rather takes the course represented by the equation  $3\text{KNCO} + 3\text{KOH} = \text{K}_2\text{CN}_2 + 2\text{K}_2\text{CO}_3 + \text{NH}_3$ , for it has been found in this Laboratory that ammonia is liberated during the reaction.

<sup>34</sup> Drechsel, *J. prakt. Chem.*, [2] 16, 206 (1877).

into calcium cyanamide and carbon dioxide. The equation  $\text{Ca}(\text{NCO})_2 = \text{CaCN}_2 + \text{CO}_2$  represents the conversion of a mixed aquo ammono-carbonate into an ammono carbonate by the elimination of carbonic anhydride, a reaction which is analogous to that which takes place on similarly exposing potassium pyrosulfate to a high temperature.

The fusion of any carbonic acid or carbonate whatever with excess of sodium amide, the caustic soda of the ammonia system, results in the formation of the disodium salt of cyanamide. This general statement includes the action of sodium amide on carbon dioxide and sodium carbonate, the anhydride and sodium salt, respectively, of aquo carbonic acid; on urea, a mixed aquo ammono carbonic acid, and on sodium cyanate and sodium carbamate, salts of aquo ammono carbonic acids; on thio-urea, a thio ammono carbonic acid and on sodium thiocyanate, a salt of a thio ammono carbonic acid and on any one of the ammono carbonic acids listed in the scheme at the beginning of this paper.

### Dicyanimide



Aqueous solutions of dicyanimide<sup>34a</sup> have been prepared by decomposing silver dicyanimide, in suspension in water, by means of hydrogen sulfide. On evaporation of the strongly acid solution thus obtained continuously deposited white, flocculent material of undetermined composition. The moderately concentrated solution solidified to a jelly-like mass which dried to an amorphous colorless powder. Analyses failed to identify this powder as a pure compound.

Calc. for  $\text{HC}_2\text{N}_3$ : C, 35.8; H, 1.5; N, 62.5. Found: C, 30.2 to 32.2; H, 2.2 to 3.0, in 5 different preparations; N, 56.1 and 59.3.

That the product thus obtained was nevertheless composed largely of dicyanimide was shown by the preparation of the potassium and barium salts of dicyanimide from the crude acid in the manner described below.

The impure acid dissolves readily in warm water. When such a solution is heated in a closed tube to  $150^\circ$  for a time, the acid is completely hydrolyzed to carbon dioxide and ammonia. On heating the crude material in a dry state considerable quantities of ammonia and other volatile products are driven off, leaving a yellow residue of melon.

Calc. for  $(\text{HC}_2\text{N}_3)_x$ : C, 35.8, H, 1.5. Found: C, 35.7; H, 1.9.

**Sodium Dicyanimide**,  $\text{NaC}_2\text{N}_3$  and  $\text{NaC}_2\text{N}_3 \cdot \text{H}_2\text{O}$ .—This ammono carbonate of sodium has been prepared by two independent methods, first by the action of fused sodium amide on melon, and second, by heating a mixture of sodium cyanide and mercuric cyanide.

*First Method.*—On the assumption that the ammono carbonic acids may be looked upon as carbonic nitride ammonated in successive steps

<sup>34a</sup> This ammono carbonic acid has not hitherto been prepared.

from hydromelonic acid,  $\text{NH}_3 \cdot 3\text{C}_2\text{N}_4$ , through to guanidine,  $5\text{NH}_3 \cdot \text{C}_2\text{N}_4$ , just as in accordance with the binary theory of Berzelius the phosphoric acids are phosphorus pentoxide combined respectively with 1, 2 and 3 molecules of water, it appeared reasonable to expect that the action of fused sodium amide on carbonic nitride would result in the formation of the sodium salt of hydromelonic acid, dicyanimide or cyanamide, depending upon the relative quantities of the two substances entering into the reaction. Since carbonic nitride is an unknown compound, melon was used in its stead in the experiments described (p. 506).

Melon dissolves readily in fused sodium amide. With the latter in excess disodium cyanamide is formed. When the reaction is carried out by dissolving an amount of melon slightly less than that required by the equation,  $x\text{NaNH}_2 + (\text{HC}_2\text{N}_2)_x = x\text{NaC}_2\text{N}_2 + x\text{NH}_3$ , a good yield of sodium dicyanimide has been obtained. Attempts to prepare the sodium salt of Liebig's hydromelonic acid by adding melon to fused sodium amide in the proportion required by the equation,  $6\text{NaNH}_2 + 3\text{H}_3\text{C}_2\text{N}_3 = 2\text{Na}_3\text{C}_3\text{N}_{13} + 7\text{NH}_3$  have given unsatisfactory results. From the aqueous solution of such melts the reaction product separated in a bulky non-crystalline form of variable sodium content. Some of the solutions solidified to a gelatinous mass on cooling.

The following described procedure has been found to give a satisfactory yield of pure sodium dicyanimide.

In a capacious gold crucible 10 g. of sodium amide and 10 g. of melon are heated together out of contact with the air (conveniently in an atmosphere of ammonia) until the reaction mixture is completely fluid. Heating is continued until all the melon is dissolved but no longer, for the reason that the yield is thereby diminished. After cooling the cake is placed in water in which it gradually disintegrates. The product is then transferred to a filter and separated by suction into a solution containing sodium cyanamide and sodium cyanide, and a solid residue of crude sodium dicyanimide. The latter is dissolved in hot water and the solution thus formed set aside to crystallize. A bulky crop of fine needle-like crystals separates after a time. Further quantities of the salt separate from the mother liquor on the addition of alcohol. In one experiment the salt separated from solution in the form of colorless, granular crystals.

The empirical composition of sodium dicyanimide is established by the analytical results given herewith.

I. Of a specimen of the salt crystallized once from the crude product 0.2017 g. heated to  $160^\circ$  lost 0.0327 g. of water and gave 0.1360 g. of  $\text{Na}_2\text{SO}_4$ . II. Four separate preparations were united and recrystallized. Of this specimen 0.2423 g. lost 0.0402 g. of water at  $160^\circ$  and gave 0.1607 g. of  $\text{Na}_2\text{SO}_4$ . III. Another preparation purified by recrystallization was heated in a vacuum to the temperature at which the soft glass container began to collapse. The specimen, which weighed 0.6002 g., lost during this treatment 0.1008 g. of water; 0.2052 g. of this dry salt on combustion gave 0.0050 g. of  $\text{H}_2\text{O}$  and 0.2042 g. of  $\text{CO}_2$ . IV. A nitrogen determination by the absolute method of Dumas was made on still another preparation; 0.1072 g. of the hydrated salt gave 37.4 cc. of N measured over water at  $22^\circ$  and 762 mm. barometric pressure (uncorr.). Calc. for  $\text{NaC}_2\text{N}_2 \cdot \text{H}_2\text{O}$ : Na, 21.5; C, 22.4; N, 39.3;  $\text{H}_2\text{O}$ ,

16.8. Found: Na, (I) 21.8, (II) 21.5; N, (IV) 39.3; H<sub>2</sub>O, (I) 16.2, (II) 16.6, (III) 16.8. Calc. for NaC<sub>2</sub>N<sub>2</sub>: C, 27.0. Found: C, (III) 27.2; H, (III) 0.3.

*Second Method.*—The reaction upon which the second method for the preparation of sodium dicyanimide is based is represented by the scheme  $\text{NaNc} + \text{C}_2\text{N}_2 \rightarrow \text{NaN}(\text{CN})_2$ . When sodium cyanide is heated in contact with cyanogen the former is nitridized to sodium dicyanimide while the latter undergoes reduction probably to carbon, possibly to carbonous nitride, although as a matter of fact the products of such reduction have not been isolated.

The clue to this method for the preparation of sodium dicyanimide goes back to Bannow<sup>25</sup> who, by extracting the melt formed by heating a mixture of potassium cyanide and mercuric cyanide, obtained a solution from which ammoniacal silver nitrate precipitated a compound of the formula  $\text{AgC}_2\text{N}_2$ . Bannow apparently also had the potassium salt of dicyanimide in his hands but no analytical data appear in his papers in support of this supposition.

After several unsuccessful attempts to isolate the potassium salt, following Bannow's directions, the following procedure was found to give a satisfactory yield of sodium dicyanimide.

Thirty g. of mercuric cyanide and 15 g. of sodium cyanide were thoroughly ground together and the mixture thus formed was heated in a glass retort until all the mercury was driven off. The residue was placed in a deep porcelain crucible and heated to complete fusion out of contact with the air. The cooled melt covered with water rapidly disintegrated. The solution, rich in sodium cyanide, was separated from the undissolved portion which latter was then dissolved in hot water. To the filtered solution alcohol was added until turbidity appeared. Then on standing a crop of yellow crystals separated, of which 0.1713 g. dried at 200° gave off 0.0272 g. of water and on treatment with sulfuric acid yielded 0.1099 g. of Na<sub>2</sub>SO<sub>4</sub>. Calc. for NaC<sub>2</sub>N<sub>2</sub>.H<sub>2</sub>O: Na, 21.5; H<sub>2</sub>O, 16.8. Found: Na, 20.9; H<sub>2</sub>O, 15.9.

The yellow salt was then heated to fusion in a platinum crucible, cooled and recrystallized. A crop of well-formed colorless crystals resulted; 0.1331 g. of the salt dried at 200° gave 0.1044 g. of Na<sub>2</sub>SO<sub>4</sub>. Calc. for NaC<sub>2</sub>N<sub>2</sub>: Na, 25.8. Found: 25.5. 0.1901 g. of the crystallized salt lost 0.0320 g. of H<sub>2</sub>O on heating to 200° and gave 0.1227 g. of Na<sub>2</sub>SO<sub>4</sub>. Calc. for NaC<sub>2</sub>N<sub>2</sub>.H<sub>2</sub>O: Na, 21.5; H<sub>2</sub>O, 16.8. Found: Na, 21.0; H<sub>2</sub>O, 16.8.

Sodium dicyanimide is moderately soluble in cold water and abundantly soluble in the hot solvent. It is also readily soluble in liquid ammonia. It is insoluble in alcohol. At temperatures around 160° it loses its water of crystallization. The anhydrous salt then resists further change up to the temperature at which soda glass begins to soften. Heated to dull redness out of contact with air it is decomposed into sodium cyanide, cyanogen and nitrogen. In contact with air it is converted into sodium carbonate. Boiled with aqueous sodium hydroxide solution it yields as final products sodium carbonate and ammonia. Heated with water alone in a sealed tube it is converted into sodium carbonate, carbon dioxide and ammonia.

**Monosodium Tri-dicyanimide**,  $\text{NaH}_2(\text{C}_2\text{N}_2)_3$  and  $\text{NaH}_3(\text{C}_2\text{N}_2)_3 \cdot 2\text{H}_2\text{O}$ .—Monomolecular formulas for dicyanimide and its sodium salt have been

<sup>25</sup> Bannow, *Ber.*, 4, 253 (1871); 13, 2201 (1880).



used in the preceding discussion for the simple reason that the real molecular weights of these substances are unknown. It appears, however, with the preparation of an acid salt of the composition represented by the formula  $\text{NaH}_2\text{C}_6\text{N}_9$ , that the free acid is a trimer of dicyanimide. In view of the ease with which cyanamide undergoes polymerization to dicyanodiamide and thence to melamine it would not be surprising to find an even greater tendency to characterize the nearly related dicyanimide.

**Preparation I.**—A solution of 2 g. of  $\text{NaC}_2\text{N}_3 \cdot \text{H}_2\text{O}$  in about 10 cc. of water was poured into an equal volume of glacial acetic acid. After standing for a short time a crop of beautiful crystals was obtained. 0.2752 g. of the salt dried in an desiccator lost 0.0378 g. of  $\text{H}_2\text{O}$  at  $200^\circ$  and gave 0.0780 g. of  $\text{Na}_2\text{SO}_4$ .

**Preparation II.**—In a second experiment carried out in the same manner excepting that hydrochloric acid was substituted for glacial acetic acid, a crop of crystals was obtained, 0.1753 g. of which lost 0.0235 g. of  $\text{H}_2\text{O}$  at  $200^\circ$  and gave 0.0483 g. of  $\text{Na}_2\text{SO}_4$ . Calc. for  $\text{NaH}_2\text{C}_6\text{N}_9 \cdot 2\text{H}_2\text{O}$ : Na, 8.9;  $2\text{H}_2\text{O}$ , 13.9. Found: Na, (I) 9.2, (II) 8.9;  $\text{H}_2\text{O}$ , (I) 13.7, (II) 13.4.

**Other Metallic Salts of Dicyanimide.**—Although the acid properties of dicyanimide are presumably established with a sufficient degree of certainty by the work just described, it nevertheless seemed worth while to confirm this conclusion by the preparation of a limited number of salts of other metals.

**Potassium Dicyanimide,  $\text{KC}_2\text{N}_3$ .**—A portion of a solution of dicyanimide prepared by the action of hydrogen sulfide on silver dicyanimide was neutralized with potassium hydroxide. On adding alcohol until a slight turbidity appeared and allowing the solution to stand for a time a bulky crop of crystals of the potassium salt of dicyanimide was obtained. 0.1087 g. of the salt dried at  $200^\circ$  gave 0.0902 g. of  $\text{K}_2\text{SO}_4$ .

In a second experiment a portion of the dry crude acid was dissolved in water and neutralized by potassium hydroxide. By manipulating this solution as described above a crop of well-formed crystals was obtained. 0.1235 g. dried at  $200^\circ$  gave 0.1014 g. of  $\text{K}_2\text{SO}_4$ . Calc. for  $\text{KC}_2\text{N}_3$ : K, 37.2. Found: (I) 37.2, (II) 36.9.

**Silver Dicyanimide,  $\text{AgC}_2\text{N}_3$ .**—On adding silver nitrate to a solution of sodium dicyanimide the silver salt separates as a pure white, very bulky precipitate insoluble either in aqua ammonia or dil. nitric acid. When dried the precipitate shrinks to hard, more or less strongly discolored masses. The composition of the salt is shown by the observations, first, that somewhat more than an equivalent quantity of silver nitrate added to a solution of 2 g. of sodium dicyanimide gave a precipitate which, after thorough washing and drying, weighed 3.21 g. (calc. 3.26 g.), and second, that 0.2106 g. of the salt on ignition left 0.1297 g. of silver. Calc. for  $\text{AgC}_2\text{N}_3$ : Ag, 62.0. Found: 61.7.

**Magnesium Dicyanimide,  $\text{Mg}(\text{C}_2\text{N}_3)_2$  and  $\text{Mg}(\text{C}_2\text{N}_3)_2 \cdot 6\text{H}_2\text{O}$ .**—To a solution containing 1 g. of sodium dicyanimide, an equivalent amount of magnesium sulfate was added. From the concentrated solution well-formed crystals separated. 0.1085 g. of the salt heated to  $160^\circ$  lost 0.0441 g. of  $\text{H}_2\text{O}$  and gave 0.0454 g. of  $\text{Mg}_3\text{P}_2\text{O}_7$ . Calc. for  $\text{Mg}(\text{C}_2\text{N}_3)_2 \cdot 6\text{H}_2\text{O}$ : Mg, 9.2;  $6\text{H}_2\text{O}$ , 40.8. Found: Mg, 9.1;  $\text{H}_2\text{O}$ , 40.7.

**Barium Dicyanimide,  $\text{Ba}(\text{C}_2\text{N}_3)_2$  and  $\text{Ba}(\text{C}_2\text{N}_3)_2 \cdot 3\text{H}_2\text{O}$ .**—Half a g. of sodium dicyanimide and an equivalent quantity of barium bromide were brought together in aqueous solution. After a short time the solution set to a solid mass of needle-like crystals. Of the air-dried salt 0.1509 g. lost 0.0249 g. of  $\text{H}_2\text{O}$  at  $160^\circ$  and gave 0.1069

g. of  $\text{BaSO}_4$ . Calc. for  $\text{Ba}(\text{C}_2\text{N}_2)_2 \cdot 3\text{H}_2\text{O}$ : Ba, 42.4;  $\text{H}_2\text{O}$ , 16.7. Found: Ba, 41.8;  $\text{H}_2\text{O}$ , 16.5.

A second specimen of the salt was prepared by neutralizing a solution of crude dicyanimide, prepared in the manner already described, with barium hydroxide solution. 0.1455 g. of the salt dried at  $160^\circ$  gave 0.1228 g. of  $\text{BaSO}_4$ . Calc. for  $\text{Ba}(\text{C}_2\text{N}_2)_2$ : Ba, 51.0. Found: 49.7.

**Cupric Dicyanimide**,  $\text{Cu}(\text{C}_2\text{N}_2)_2$  and  $\text{Cu}(\text{C}_2\text{N}_2)_2 \cdot 3\text{H}_2\text{O}$ .—Addition of cupric sulfate to a solution of sodium dicyanimide gave a dark green insoluble precipitate. 0.1024 g. of the salt dried at  $100^\circ$  gave 0.0328 g. of  $\text{CuO}$ . A second portion weighing 0.1004 g. lost 0.0216 g. of  $\text{H}_2\text{O}$  on heating to  $160^\circ$  and gave 0.0324 g. of  $\text{CuO}$ . Calc. for  $\text{Cu}(\text{C}_2\text{N}_2)_2 \cdot 3\text{H}_2\text{O}$ : Cu, 25.5;  $3\text{H}_2\text{O}$ , 21.6. Found: Cu, (I) 25.6, (II) 25.8;  $\text{H}_2\text{O}$ , (II) 21.5.

**Nickel Dicyanimide**,  $\text{Ni}(\text{C}_2\text{N}_2)_2 \cdot 3\text{H}_2\text{O}$ .—Addition of an equivalent quantity of nickel sulfate to a solution of 0.50 g. of sodium dicyanimide gave a beautiful green insoluble precipitate. 0.1084 g. of the vacuum-dried salt gave 0.0335 g. of  $\text{NiO}$ ; a second portion of 0.1590 g. gave 0.0486 g. of  $\text{NiO}$ . Calc. for  $\text{Ni}(\text{C}_2\text{N}_2)_2 \cdot 3\text{H}_2\text{O}$ : Ni, 24.0. Found: Ni, 24.2, 24.0. The salt could not be satisfactorily dehydrated by heating.

### Dicyanodiamide



In view of its position in the series of ammono carbonic acids, cyanamide might be expected to undergo de-ammonation to form dicyanimide and possibly even carbonic nitride. As a matter of fact, however, the reactions which take place when cyanamide is heated, follow another course, namely, polymerization successively to dicyanodiamide and melamine, the latter then losing ammonia after the manner already described. The dimerization of cyanamide to dicyanodiamide may be looked upon as a process analogous to the hydration of cyanamide to urea or its ammonation to guanidine. In the formation of dicyanodiamide a second molecule of cyanamide functions as water does in the formation of urea and as ammonia does in the formation of guanidine. Dicyanodiamide is a neutral substance which does not form salts in aqueous solution though indications of its acid nature are on record to the extent that a sodium<sup>36</sup> and a silver salt are known. The reactions described below, carried out in liquid ammonia as solvent, bring out clearly the acid properties of this ammono carbonic acid.

**Dipotassium Dicyanodiamide**,  $\text{K}_2\text{H}_2\text{C}_2\text{N}_4$ .—This salt is formed in accordance with the equation  $\text{H}_4\text{C}_2\text{N}_4 + 2\text{KNH}_2 = \text{K}_2\text{H}_2\text{C}_2\text{N}_4 + 2\text{NH}_3$ , when potassium amide in excess and dicyanodiamide are brought together in liquid ammonia solution. It was obtained as a very slightly soluble crystalline product.

**Preparation I.**—In order to replace as much of the hydrogen as possible in the tetrabasic acid a solution containing 0.40 g. of dicyanodiamide was added to a solution containing a generous excess of potassium amide. An amorphous precipitate was formed

<sup>36</sup> The sodium salt was obtained by bringing together sodium ethylate and dicyanodiamide in absolute alcohol solution (Bamberger, *Ber.*, 16, 1461 (1883)).

which, after standing over night in contact with the mother liquor, changed to a crystalline product. The salt was washed sparingly with the object in view of avoiding possible ammonolysis of a hypothetical tri- or tetrapotassium salt. The salt was dried at 20° in a vacuum. The dry salt was treated first with water, then dissolved in dil. hydrochloric acid preparatory to analysis. The specimen weighed 0.4452 g. One half gave 0.2430 g. of  $K_2SO_4$ . The other half gave 0.0777 g. of N. Calc. for  $K_2H_3C_2N_4$ : K, 48.8; N, 35.0. Found: K, 48.8; N, 35.0.

Since the dipotassium salt of sharply definite composition was obtained in the presence of a large excess of potassium amide it is obvious that in liquid ammonia solution not more than two atoms of hydrogen are replaceable by metals.

**Monopotassium Dicyanodiamide,  $KH_3C_2N_4$ .**—The monopotassium salt of dicyanodiamide is formed when equimolecular quantities of dicyanodiamide and potassium amide are brought together in liquid ammonia solution. The salt crystallizes beautifully and is fairly soluble.

**Preparation I.**—To a solution containing 0.40 g. of dicyanodiamide the potassium amide from 0.19 g. of potassium (1 equivalent) was added. The precipitate which formed on the addition of each portion of potassium amide solution dissolved completely to a clear colorless solution. On evaporating the solution to a fairly high concentration the monopotassium salt separated as a crop of well-formed crystals. The product was drained of mother liquor and washed twice with small quantities of pure solvent. Dried at 20° the specimen weighed 0.5107 g. One half gave 0.1810 g. of  $K_2SO_4$ . The other half gave 0.1170 g. of N. Calc. for  $KH_3C_2N_4$ : K, 32.0; N, 45.8. Found: K, 31.8; N, 45.7.

**Magnesium Dicyanodiamide,  $Mg(H_3C_2N_4)_2 \cdot 2NH_3$ .**—The magnesium salt of dicyanodiamide has been prepared by the action of a solution of the acid on metallic magnesium in accordance with the equation,  $Mg + 2H_3C_2N_4 = Mg(H_3C_2N_4)_2 + H_2$ .

**Preparation I.**—A solution of 0.60 g. of dicyanodiamide was poured upon 0.070 g. of magnesium metal. The metal was immediately attacked with the evolution of hydrogen and was completely dissolved after the lapse of half an hour. The solution was poured from a small quantity of white insoluble material and evaporated to a rather high degree of concentration when well-formed crystals separated. Once formed, the crystals seemed to be practically insoluble. The crop of crystals was washed, then dried in a vacuum at 20°. The weight of the specimen was 0.5132 g. One half gave 0.1372 g. of  $MgSO_4$ . The other half gave 0.1600 g. of N. Calc. for  $Mg(H_3C_2N_4)_2 \cdot 2NH_3$ : Mg, 10.8; N, 62.4. Found: Mg, 10.8; N, 62.5.

**Calcium Dicyanodiamide,  $Ca(H_3C_2N_4)_2 \cdot NH_3$  and  $Ca(H_3C_2N_4)_2 \cdot 4NH_3$ .**—This salt is formed by the action of a liquid ammonia solution of dicyanodiamide on either metallic calcium or calcium amide. It separates from very concentrated solutions at low temperatures with 4 molecules of ammonia of crystallization, three of which are lost on heating to 50°.

**Preparation I.**—The blue color of a solution of metallic calcium in liquid ammonia solution was instantly discharged when the calcium solution was poured into one of dicyanodiamide. The products of the reaction were an insoluble white portion and an extremely soluble salt which remained as a viscous mass when the solvent was distilled at laboratory temperature. The specimen was lost by the explosion of the reaction tube.

**Preparation II.**—In the presence of platinum black 0.133 g. of metallic calcium was converted into calcium amide which is practically insoluble in liquid ammonia.

On pouring a solution containing 0.56 g. of the acid upon the amide the latter went rapidly into solution excepting a white insoluble residue, the nature of which was not determined. The solution was poured from this residue and evaporated at low temperature to crystallization. A bulky crop of crystals was obtained. The salt, which is very soluble, exhibits the phenomenon of supersaturation to a surprising degree. The mother liquor in considerable quantity was drained from the crop of crystals which were then dried in a vacuum at  $-33^{\circ}$ . The weight was 0.4444 g. After heating to  $50^{\circ}$  the weight was 0.3574 g. One fifth gave 0.0395 g. of N. Four fifths gave 0.1764 g. of  $\text{CaSO}_4$ . Calc. for  $\text{Ca}(\text{H}_2\text{C}_2\text{N}_4)_2\text{NH}_3$ : Ca, 17.9; N, 56.4. Found: Ca, 18.1, N, 55.3. Calc. for  $\text{Ca}(\text{H}_2\text{C}_2\text{N}_4)_2\text{NH}_3 \cdot 3\text{NH}_3$ :  $3\text{NH}_3$ , 18.6. Found: 19.5.

The high degree of solubility and the bulky nature of this salt made its separation and proper drying a matter of considerable difficulty. The attempt was not made to obtain an ammonia-free salt.

**Monosilver Dicyanodiamide**,  $\text{AgH}_2\text{C}_2\text{N}_4$ ,  $\text{AgH}_2\text{C}_2\text{N}_4\text{NH}_3$  and  $\text{AgH}_3\text{C}_2\text{N}_4 \cdot 2\text{NH}_3$ .—Monosilver dicyanodiamide is formed by the action of a solution of the acid on either silver amide of silver oxide. It was obtained well-crystallized with two molecules of ammonia. It loses one molecule of ammonia at  $40^{\circ}$ , melts at about  $60^{\circ}$  and gives up all its ammonia at a somewhat higher temperature.

**Preparation I.**—Silver amide prepared from 0.42 g. silver nitrate dissolved rapidly and completely in a solution containing 0.21 g. of dicyanodiamide. On evaporating the solution to proper concentration a crop of crystals separated on the walls and bottom of the tube. After washing the crystals with several small portions of pure solvent they were dried in a vacuum at  $-33^{\circ}$ . Heated to  $45^{\circ}$  the specimen lost 0.0204 g. of ammonia and weighed 0.2707 g. It gave 0.0938 g. of N and 0.1768 g. of  $\text{AgCl}$ . Calc. for  $\text{AgH}_2\text{C}_2\text{N}_4 \cdot 2\text{NH}_3$ : Ag, 48.0; 5N, 31.2;  $1\text{NH}_3$ , 7.5. Found: Ag, 45.8, N, 32.2;  $\text{NH}_3$ , 7.0.

**Preparation II.**—Silver amide from 0.50 g. of silver nitrate was dissolved in a solution containing 0.25 g. of the ammono carbonic acid. On concentrating the solution a crop of crystals was obtained which was washed and dried in the usual manner. Since the analysis of the first preparation showed that not all the ammonia of crystallization was removed, the preparation was exposed to a higher temperature in this experiment. At  $60^{\circ}$  the crystals melted to a viscous frothy mass which lent itself illly to complete de-ammonation. Dried at  $-33^{\circ}$  in a vacuum the salt weighed 0.4213 g. After heating to  $70^{\circ}$  it weighed 0.3613 g. and gave 0.1026 g. of N and 0.2685 g. of  $\text{AgCl}$ . Calc. for  $\text{AgH}_2\text{C}_2\text{N}_4 \cdot 2\text{NH}_3$ : Ag, 48.0; 4N, 24.8;  $2\text{NH}_3$ , 15.1. Found: Ag, 48.0; N, 24.4;  $\text{NH}_3$ , 14.3.

**Preparation III.**—A specimen of silver dicyanodiamide was also made by the action of a liquid ammonia solution of 0.20 g. of dicyanodiamide on 0.60 g. of silver oxide. Since silver oxide was in excess of the amount necessary for the formation of the monosilver salt, a portion only of the silver oxide went into solution. The solution was transferred to the second leg of the reaction tube and the residue then extracted several times with pure solvent. The crop of crystals obtained when dried at laboratory temperature weighed 0.1300 g. and gave 0.0824 g. of  $\text{AgCl}$  and 0.0473 g. of N. Calc. for  $\text{AgH}_2\text{C}_2\text{N}_4 \cdot 2\text{NH}_3$ : Ag, 48.0; N, 47.3. Found: Ag, 47.7; N, 36.4.

**Disilver Dicyanodiamide**,  $\text{Ag}_2\text{H}_2\text{C}_2\text{N}_4$ .—The grayish residue from which the above preparation was extracted was in all probability impure disilver dicyandiamide, for after washing and drying it was found to contain Ag, 69.2; N, 18.1. Calc. for  $\text{Ag}_2\text{H}_2\text{N}_4$ : Ag, 72.5; N, 18.8.

**Cuprous Dicyanodiamide**,  $\text{CuH}_3\text{C}_2\text{N}_4 \cdot 2\text{NH}_3$ .—Cuprous dicyanodiamide

is extremely soluble in liquid ammonia and crystallizes only from very concentrated solutions at low temperatures. It separates in the form of colorless crystals containing two molecules of ammonia of crystallization which are incompletely lost on heating. The merest trace of air gaining entrance to the preparation tube imparts a blue color to the salt.

**Preparation I.**—The cuprous amide obtained from 1.00 g. of  $\text{Cu}(\text{NO}_3)_2 \cdot 4\text{NH}_3$  was treated with a solution containing for each atom of copper 2 molecules of the acid. The amide dissolved slowly giving a slightly blue solution. The color was completely discharged by allowing the solution to stand in contact with bits of copper foil for a few hours. The extremely soluble salt separated from the highly concentrated solution on cooling strongly. The crystals were merely drained from mother liquor for analysis. Adhering mother liquor readily accounts for the low content of copper and the high nitrogen found on analysis. The salt dried at  $20^\circ$  in a vacuum weighed 0.5198 g. One half gave 0.1092 g. of  $\text{CuO}$ . The other half gave 0.1237 of N. Calc. for  $\text{Cu}_2\text{C}_2\text{N}_4 \cdot 2\text{NH}_3$ : Cu, 35.2; N, 46.6. Found: Cu, 33.6; N, 47.6.

**Preparation II.**—Again the cuprous amide from 1.00 g. of  $\text{Cu}(\text{NO}_3)_2 \cdot 4\text{NH}_3$  was dissolved in a solution of excess of dicyanodiamide. The blue color due to the presence of a small amount of cupric salt was removed by the reducing action of copper foil. The crop of crystals obtained from the very concentrated cold solution was recrystallized for analysis. Dried in a vacuum at  $-33^\circ$  the specimen weighed 0.2458 g. On heating slightly above laboratory temperature the crystallized salt fused to a viscous liquid which changed to a mass of froth as the escaping ammonia was pumped off. Dried finally at  $40^\circ$  the specimen weighed 0.2087 g. One half gave 0.0436 g. of N. The other half gave 0.0530 g. of  $\text{CuO}$ . Calc. for  $\text{CuH}_2\text{C}_2\text{N}_4 \cdot 2\text{NH}_3$ : Cu, 35.2; total N, 46.7;  $2\text{NH}_3$ , 18.8. Found: Cu, 34.6; total N, 47.9;  $\text{NH}_3$ , 15.1.

### Melamine



Melamine, a trimer of cyanamide, is a basic substance which forms salts by direct union with acids. Contrary to the statements<sup>37</sup> frequently made to the effect that melamine is a strong monacid base, it is, as a matter of fact, a very weak base. Its aqueous solution has no effect on litmus or phenolphthalein while, as observed by Liebig,<sup>38</sup> its salts all show an acid reaction towards vegetable colors.

The specimen of melamine used for making the potassium salt described below was obtained in the form of beautifully developed crystals by heating a liquid ammonia solution of dicyanodiamide at a temperature of  $100^\circ$  for several hours.

The identity of the product as melamine was established by observations on its solubility in water and in liquid ammonia, on its crystal form and on its behavior on heating. Its purity was shown by a combustion. 0.2070 g. of substance gave 0.0872 g. of  $\text{H}_2\text{O}$  and 0.2169 g. of  $\text{CO}_2$ . Calc. for  $\text{H}_6\text{C}_3\text{N}_6$ : H, 4.7; C, 28.6. Found: H, 4.7; C, 28.6.

<sup>37</sup> Beilstein "Handbuch der organischen Chemie," Leopold Voss, Hamburg and Leipzig, 1, 1443 (1893); Meyer and Jacobson, "Lehrbuch d. organischen Chemie," Veit and Company, Leipzig, 2nd Ed., 1, 2, 1337 (1913).

<sup>38</sup> Liebig, *Ann.*, 10, 19 (1834).

Melamine is moderately soluble in liquid ammonia at laboratory temperature. On cooling to  $-33^{\circ}$  most of the solute separates from solution in the form of beautiful crystals.

**Tripotassium Melamine**,  $K_3H_3C_3N_6$ .—This salt has been obtained in the form of a practically insoluble microcrystalline powder by the action of potassium amide on melamine in solution in liquid ammonia in accordance with the reaction represented by the equation,  $H_3C_3N_6 + 3KNH_2 = K_3H_3C_3N_6 + 3NH_3$ . It is vigorously hydrolyzed into potassium hydroxide and melamine in the presence of water.

**Preparation I.**—In one leg of a reaction tube was contained 1.20 g. of melamine in solution in liquid ammonia, in the other a solution of a large excess of metallic potassium. A portion of the metal solution poured into the solution of melamine lost its blue color instantly, a behavior which shows the acid properties of melamine. The reaction tube was then allowed to stand until the metal in solution, in the presence of a trace of platinum black, was converted into a solution of potassium amide. Successive additions of melamine to this solution gave a colorless, bulky precipitate which changed rapidly to a microcrystalline powder. The washed salt dried in a vacuum at  $-33^{\circ}$  showed no loss in weight on warming to laboratory temperature. The dried salt was hydrolyzed by the addition of water and the hydrolytic products resulting were dissolved in dil. hydrochloric acid preparatory to analysis. The preparation weighed 0.3897 g. One half gave 0.2120 g. of  $K_2SO_4$ . The other half gave 0.0673 g. of N. Calc. for  $K_3H_3C_3N_6$ : K, 48.8; N, 34.9. Found: K, 48.8; N, 34.6.

**Preparation II.**—Tripotassium melamine prepared as described above not only has the same empirical composition as dipotassium dicyanodiamide but it is also very slightly soluble and was obtained as a microcrystalline product indistinguishable in appearance from the latter salt through the walls of the reaction tube. Since there thus appeared the possibility that melamine in the presence of potassium amide might be converted into dicyanodiamide or even into cyanamide (by fusion with sodium amide, it will be recalled, both of these substances are converted into sodium cyanamide) a second specimen of the tripotassium salt of melamine was prepared, decomposed by the action of water, the hydrolytic product other than potassium hydroxide recovered and identified as melamine. The potassium hydroxide solution was neutralized with sulfuric acid and evaporated to dryness. Ignition of the residue gave 0.1188 g. of potassium sulfate. The specimen weighed 0.1108 g. Calc. for  $K_3H_3C_3N_6$ : K, 48.8. Found: 48.2.

**Monopotassium Melamine**,  $KH_3C_3N_6 \cdot NH_3$ .—This salt separates as a very slightly soluble precipitate when potassium amide is added to an excess of melamine in liquid ammonia solution.

**Preparation I.**—To a solution containing 0.30 g. of melamine, a potassium amide solution prepared from 0.092 g. of metallic potassium was gradually added. Each addition of the amide gave a gelatinous insoluble mass which rapidly disintegrated and settled to the bottom of the tube in the form of a fairly compact precipitate. Five extractions of this precipitate carried out in the manner which has been described elsewhere gave a specimen of minute brilliant crystals covering the walls and bottom of the reaction tube. The specimen was washed, then dried in a vacuum at  $20^{\circ}$ . Its weight was 0.0950 g. For analysis the salt was treated with water, then dissolved in dil. hydrochloric acid. One half gave 0.0231 g. of  $K_2SO_4$ . The other half was inadvertently lost.

**Preparation II.**—The precipitate from which the preceding preparation was extracted was washed in the usual manner and prepared for analysis as described above. From a portion of the precipitate the melamine was recovered and identified. The remaining portion was dried in a vacuum at 20° and submitted to analysis. One half of the specimen which weighed 0.1553 g. gave 0.0382 g. of  $K_2SO_4$ , the other half gave 0.0417 g. of N. Calc. for  $KH_2C_3N_3.NH_3$ : K, 21.6; N, 54.1. Found: K, (I) 21.8; (II) 22.1; N, (II) 53.7.

The ease with which these potassium salts have been obtained make it practically certain that melamine salts of other metals may be prepared.

Zimmermann<sup>39</sup> obtained a disilver salt of melamine by treating melamine disilver nitrate with aqua ammonia.

#### Melam $H_3C_3N_{11}$

#### Melem $H_6C_6N_{10}$

These compounds are said to be present in Liebig's crude melam, the residue remaining after heating ammonium thiocyanate at a temperature around 300° to 360° so long as volatile products are given off. They are colorless, amorphous, insoluble substances, the existence of which as chemical individuals is open to some doubt.

#### Melon



This name was given by Liebig to the yellow, amorphous, insoluble residue obtained by heating to redness the yellow precipitate formed by the action of chlorine on a solution of potassium thiocyanate. The compound was first observed by Berzelius who obtained it by heating mercuric thiocyanate. Formed in this manner it is familiar as the substance of the so-called Pharaoh's serpents. Melon<sup>40</sup> is left behind as the final de-ammonation product on heating any one of the previously discussed ammono-carbonic acids. It is also formed by heating urea, ammonium thiocyanate and a large number of other mixed carbonic acids. Heated with water in a sealed tube to 200° for several hours it is hydrolyzed through a considerable number of aquo ammono carbonic acids finally to carbon dioxide

<sup>39</sup> Zimmermann, *Ber.*, 7, 287(1874). (Not volume 9, as given in Beilstein.)

<sup>40</sup> Although Laurent and Gerhardt (*Ann. chim.*, [3] 19, 89 (1847)) and Voelckel (*Pogg. Ann.*, 62, 104 (1844)) have apparently shown melon to have the composition represented by the formula  $H_3C_3N_3$ , it is nevertheless a difficult matter to obtain the compound of sharply definite composition. Carbon and hydrogen determinations in 4 specimens of melon prepared from dicyandiamide and one from ammonium thiocyanate gave results varying from 34.9 to 36.9% of carbon and from 1.1 to 2.0 % of hydrogen. Nitrogen determinations by the method of Kjeldahl gave persistently low results varying from 61.0 to 62.8%. One nitrogen determination by the absolute method gave 62.8%. (Calc. for  $H_3C_3N_3$ : H, 1.5; C, 35.8; N, 62.7.) It is interesting to note in this connection that Liebig states in several places (*Ann.*, 50, 341 and 354 (1844); *ibid.*, 95, 258 (1855)) that he was unable to obtain melon of constant composition. Cf. Voelckel, *Pogg. Ann.*, 58, 151 (1843).

and ammonia. Melon is to be looked upon as a highly polymerized form of dicyanimide.

### Cyamelon or Hydromelonic Acid



Melon and the salts of hydromelonic acid are substances which were at one time of much theoretical importance. Their nature and, strange as it may seem, even their elementary composition were through years the subject of an acrimonious controversy between Liebig on the one side and Laurent and Gerhardt on the other,<sup>41</sup> the outcome of which, insofar as our present interest is concerned, was to show that the metallic melonates are the salts of an acid, not known in the free state excepting in solution, of the composition represented by the formula given above. It is an acid of sufficient strength to form salts in water solution and is the final known member of the series of ammono carbonic acids.

### Carbonic Nitride



One might expect to obtain carbonic nitride as the final de-ammonation product of the series of ammono carbonic acids by heating melon, but instead of losing ammonia at the high temperature required to effect any change at all it undergoes complete decomposition.<sup>42</sup> Attempts have been made in this laboratory to prepare carbonic nitride by heating mercuric thiocyanate, with results which, while far from unequivocal, show that impure specimens of carbonic nitride have passed through our hands.

Specimens of mercuric thiocyanate prepared in the usual manner were dried by long standing in a vacuum over sulfuric acid, others by heating in a vacuum at 150°. The salt was then decomposed by heat and the extremely bulky residue heated in quartz in a vacuum until free from mercuric sulfide. Six separate specimens gave on combustion 2.4, 1.5, 0.6, 0.7, 1.5 and 1.7% of hydrogen; and 40.2, 39.7, 38.4, —, 35.9 and 35.9% of carbon respectively. Calc. for  $\text{C}_2\text{N}_4$ : C, 39.1. Nitrogen determinations were more consistent. Four determinations on different specimens by the method of Dumas gave 60.4, 60.7, 58.0 and 60.6% of nitrogen, while one by the method of Kjeldahl gave 60.6%. Calc. for  $\text{C}_2\text{N}_4$ : N, 60.9. Further attempts will be made to prepare the pure compound.

### The Action of Fused Sodium Amide on the Ammono Carbonic Acids

The ammono carbonic acids constitute a series of compounds the members of which are related to each other as are the ortho-,

<sup>41</sup> In the older text-books and dictionaries of chemistry melon and related compounds were given a great deal of attention; cf. Liebig, "Traité de Chim. org.," 3rd Ed. 1845, Société Typographique Belge Adolphe Wahlenet Cie., p. 127; Gerhardt, "Traité de Chim. org.," Firman Didat Frères, Paris, 1853, vol. 1, 464, 473; Gmelin-Watts, "Handbook of Chemistry," The Cavendish Society, London, 1855, vol. 9, p. 378. In modern works of the same kind they are scarcely more than mentioned.

<sup>42</sup> There is entire disagreement concerning the products of this decomposition. Cf. Liebig, *Ann.*, 10, 5 (1834); Laurent and Gerhardt, *Ann. chim. phys.*, [3] 19, 101 (1847); Voelckel, *Pogg. Ann.*, 61, 375 (1844). Gmelin-Watts, Ref. 41, p. 381.



pyro- and metaphosphoric acids within the group of phosphoric acids or the less well defined individuals within the group of silicic acids. Accordingly, sodium ammonio carbonates of greater or less acidity<sup>43</sup> are formed by the action of fused sodium amide in excess or in dearth upon any one of the ammonio carbonic acids just as the relative proportions in which sodium hydroxide and any one of the phosphoric acids are fused together determine which of the phosphates will be formed.

Experiment has shown that disodium cyanamide is formed when sodium melonate, melon, crude melam, melamine,<sup>44</sup> dicyandiamide,<sup>44</sup> sodium dicyanimide, cyanamide or guanidine<sup>45</sup> is dissolved in an excess of fused sodium amide and inversely that disodium cyanamide is converted into sodium dicyanimide by dissolving melon in the fused salt. Attempts to carry the process to the formation of trisodium melonate have so far resulted in the formation of gelatinous products of varying composition.

In successive experiments small amounts of each of the above named substances excepting that guanidine nitrate and guanidine carbonate were used instead of guanidine itself, were added to approximately 1 g. of sodium amide maintained in a state of fusion in an atmosphere of ammonia. Each substance was observed to dissolve readily with effervescence due to the escape of ammonia, one of the products of the reaction. Each cooled melt, together with the silver boat in which the reaction was carried out, was dropped into a beaker of water. To the solution formed, strongly alkaline from the presence of sodium hydroxide and ammonia resulting from the hydrolysis of excess of sodium amide, ammoniacal silver nitrate was added with the result that in each case an abundant precipitate of disilver cyanamide was formed. The precipitates were identified as disilver cyanamide by their characteristic yellow color confirmed in one instance by noting the ready solubility of the yellow substance in dil. nitric acid and by a determination of its silver content.

### Hydrolysis of the Ammonio Carbonic Acids

The hydrolysis of calcium cyanamide to calcium carbonate and the inverse reaction, namely, the ammonolysis of calcium carbonate to calcium cyanamide have been discussed above. There remains to be given here the results of experiments which show that all the ammonio carbonic acids undergo hydrolysis to carbon dioxide and ammonia when heated in the presence of water.<sup>46</sup>

Guanidine carbonate, dicyanodiamide, melamine, melon and crude dicyanimide in half gram portions together with 5 cc. of water were sealed in 5 respective glass tubes

<sup>43</sup> Acidity is here used in the sense in which the mineralogist uses the term in describing his silicates.

<sup>44</sup> Of course in the case of these two compounds the reaction is merely one of depolymerization.

<sup>45</sup> It is interesting to note that excess of sodium amide does not form a guanidine salt. The analogous situation in the case of the phosphates is that excess of sodium hydroxide does not form a salt of the composition  $\text{Na}_3\text{PO}_4$ .

<sup>46</sup> Cf. Emich, *Monatsh.*, 9, 378 (1888).

and heated to a temperature of 200° for a day. On cooling and examining the contents of the tubes each substance was found to have been hydrolyzed completely into carbon dioxide and ammonia.

### Summary

- As is shown in the scheme at the beginning of this paper, guanidine, biguanide, cyanamide, dicyanimide, dicyanodiamide, melamine, melam, melem, melon and hydromelonic acid constitute a group of compounds which may be looked upon as ammono carbonic acids. That is to say, they are compounds related to ammonia as ordinary carbonic acid is related to water or in other words, they are carbonic acids in which nitrogen functions as oxygen does in ordinary carbonic acid.

It is pointed out that not only formally may these substances be looked upon as constituting a series of products resulting from the successive de-ammonation of an hypothetical ammono ortho carbonic acid of the formula  $C(NH_2)_4$ , but that also by processes of de-ammonation one may pass from guanidine to melon and inversely by processes of ammonation return to the first member of the group.

In face of the facts that guanidine and melamine are alkaline and dicyanodiamide is neutral in aqueous solution, it has been shown that these substances behave as acids when in solution in liquid ammonia. Guanidine for example, has been found to react with potassium amide, the caustic potash of the ammonia system, in accordance with the equation,  $H_2CN_2 + 2KNH_2 = K_2H_2CN_2 + 2NH_3$  to form a dipotassium salt.

It has been shown that the reaction whereby atmospheric nitrogen is fixed in the cyanamide process is to be looked upon as the nitridation of calcium carbide to a calcium ammono carbonate and that the production of ammonia by the action of steam on calcium cyanamide consists in the hydrolysis of calcium ammono carbonate to calcium aquo carbonate.

Dicyanimide, a hitherto unknown member of the group of ammono carbonic acids, has been prepared together with a considerable number of its metallic salts. Attempts to prepare carbonic nitride, the theoretical final de-ammonation product of the series of ammono carbonic acids, are described.

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[CONTRIBUTION FROM THE KENT CHEMICAL LABORATORY OF THE UNIVERSITY OF CHICAGO]

## TRIATOMIC HYDROGEN. II

BY GERALD L. WENDT AND ROBERT S. LANDAUER

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Since our first paper<sup>1</sup> Venkataramaiah reported<sup>2</sup> the independent discovery of the active form of hydrogen, distinguished by its ability to reduce potassium permanganate solution rapidly at room temperature. He produced it first in the alternating current corona, but made the interesting observation that it is produced in measurable quantities when oxygen is exploded in an excess of hydrogen. Since all other methods of its preparation, including those reported below, are dependent on prolonged and intense ionization of the hydrogen, this preparation by explosion is of importance in determining the mechanism of its formation.

### New Methods of Preparation

**Siemens Ozonizer.**—In view of the ready formation of the new gas by means of the electrical discharge at 10,000 to 20,000 volts and a current of 4 to 25 milli-amperes, both at atmospheric pressure and at a pressure of 4 to 8 cm. of mercury, there is little new in its successful preparation in the usual quantities of about 0.01% by means of the ordinary Siemens glass tube ozonizer, with external tin-foil electrodes. This method is simple and reliable. It is particularly effective at the temperature of boiling liquid ammonia. This method failed, however, when the ozonizer was immersed in liquid air, probably because of the increased dielectric strength of the glass walls. When metallic electrodes were inserted through the walls of the tube, the low temperature did not prevent the activation.

In this, as in all the work, the hydrogen was prepared and purified as described in the previous paper. In all cases the test for activation was the formation of hydrogen sulfide in passage of the gas over cold sulfur. In every case blank tests were made to show that the hydrogen itself, without the ionizing agent, did not attack the sulfur.

**High-frequency Discharge.**—A marked increase in the frequency and voltage of the electric discharge has no appreciable effect on the amount of activation of the hydrogen. This was shown by using the discharge from a Tesla coil consisting of a primary of one turn of heavy cable surrounding a secondary coil of 1680 turns of No. 28 enameled copper wire. The voltage from such a system is well up in the millions, and the frequency perhaps

<sup>1</sup> THIS JOURNAL, 42, 920 (1920); presented at the Philadelphia meeting, American Chemical Society, September, 1919.

<sup>2</sup> An oral communication to the Science association, Maharajah's College, Vizianagaram, S. India, January 29, 1920; printed in the *Proceedings* of the Science Association July 10, 1921; *Nature*, 106, 46 (1920).

half a million cycles per second. The secondary of the Tesla coil was connected to a large Siemens ozonizer tube, and the hydrogen passed through at velocities of 25 to 150 cc. per minute. The activation was pronounced and of the same amount as in previous experiments with lower voltages.

**Thermionic Emission.**—All ionizing agents had now proved to be successful activators with the single exception of ultra-violet light, which is but slightly absorbed in hydrogen, and an exceedingly weak source of ionization. Even Schumann rays, which are probably absorbed, showed no activation. In order to test a remaining source of ions, though weak, hydrogen was now passed over a 0.46 mm.<sup>3</sup> platinum wire maintained electrically at a temperature of about 800°. In spite of the relatively weak electron stream from such a wire, the hydrogen was activated readily.

The wire was 16 cm. long, and was welded at each end to 12 short lengths of 0.38mm. (No. 28) platinum wire, which were then sealed through the glass walls. This expedient was adopted in order to allow the protracted passage of a heavy current for maintaining the temperature of the wire without overheating the glass. The hydrogen entered at one end of the 20 cm. glass tube 15 mm. in diameter, and after passing over the wire left at the other end, passed through a coil which could be immersed in cold water and thence over the powdered sulfur and the lead acetate paper as usual. A heavy black sulfide test resulted in repeated runs of 30 minutes with a current of 10 to 12 amperes through the wire, and with a hydrogen flow of 60 cc. per minute.

The same sources of the hydrogen sulfide that needed to be eliminated were present here as in previous work, and in addition the possibility of a reaction by the heated ordinary hydrogen. Impurities were eliminated, as before, by the complete purifying system and a coil immersed in liquid air preceding the exposure to the hot wire. Thus all possible impurities except nitrogen and the gases of the helium group were excluded, and these latter cannot give the black sulfide test. Ions were again shown not to be present by passing the gas after activation through a sensitive radium emanation electroscope without any indication of conductivity.<sup>4</sup>

There remains the possibility that the hydrogen reacts because it retains a high temperature. At 200° ordinary hydrogen has an easily detectable action on sulfur. But a thermometer inserted in the side tube at the exit of the hydrogen from the hot wire tube showed a temperature of

<sup>3</sup> No. 26 B. and S. gage.

<sup>4</sup> Attention is called to an unfortunate though non-significant error in the previous paper. The sentence beginning on Line 12, p. 936, should, of course, read: "Since there are  $2.7 \times 10^{19}$  molecules in a cubic centimeter,  $8 \times 10^{12}$  molecules occupy  $3 \times 10^{-7}$  cc. and weigh slightly more than  $3 \times 10^{-11}$  g., an undetectable quantity." The same figures apply in this case, i. e., even had an easily measured number of ions been present and had they been able to react with the sulfur, which is itself more than doubtful, they could have accounted for less than 0.001% of the activity actually observed.

31°, room temperature being 27°. The long coil of thin-walled glass tubing which was placed between the hot-wire tube and the sulfur tube was then immersed in an ice-water mixture at 0°. It had no effect whatever on the action of the hydrogen on the sulfur. A thermometer placed at the exit of this coil showed a temperature of 29°. Although the heat capacity of the thermometer was undoubtedly high, runs were extended to as much as 16 hours with no change in the observations, and the time thus was ample to allow the thermometer to come into thermal equilibrium with the hydrogen in which it was bathed. That the activity of the hydrogen was due to increased temperature was, therefore, also excluded, and an active form of hydrogen remains as the only possibility.

To determine what is the activating agent in this case is a problem in electronics which we cannot attempt. There seem to be three possibilities: the thermal dissociation of hydrogen into atoms, ionization by the electron stream from the wire, and disruption by positive ions from the wire.

The calculations of Langmuir<sup>5</sup> show that thermal dissociation for a wire at less than 1000° is certainly inadequate, amounting to less than  $5.8 \times 10^{-11}\%$ . This is so small a quantity that it could not possibly account for the observed activation. The second possibility, namely, the ionization of the hydrogen by negative electrons, seems to be excluded by the work of O. W. Richardson.<sup>6</sup> Not only are few, if any, negative electrons emitted at temperatures of 800–900°, but the energy of those emitted under the conditions of our experiment must be very low, since there is no accelerating potential applied. The third possibility is also unsatisfactory, but seems at present the most plausible, namely, that positive ions are emitted from the wire and cause the ionization. Richardson has shown that at low temperatures the emission of positive ions far exceeds that of negative ions, and with larger mass the energy of these ions would perhaps be sufficient to produce ionization. Richardson assumes that the positive ions emitted are ions of the alkali metals present in the platinum as impurities. Until more evidence on ionizing potentials and thermionic emission is available, this activation by the hot wires remains to be explained.

**Nascent Hydrogen.**—According to the theory suggested in the previous paper, the triatomic modification of hydrogen is formed by ionization because the  $H_2$  molecule is not stable when one of its electrons has been torn off. Hence it splits into atoms which recombine to give triatomic molecules. If this suggestion is correct, the ozone form should be produced whenever atomic hydrogen is formed, and therefore nascent hydrogen

<sup>5</sup> Langmuir, *Trans. Am. Electrochem. Soc.*, **20**, 225 (1911); *THIS JOURNAL*, **34**, 860 (1912); **34**, 1310 (1912); **36**, 1706 (1914); **37**, 417 (1915).

<sup>6</sup> Richardson, "The Emission of Electricity from Hot Bodies," Longmans, Green and Company, 1916.

should retain a fraction of its activity after it is evolved in the gaseous form. Such an activity was, therefore, sought by three methods, but all results were negative.

First, hydrogen was produced by the solution of zinc in hydrochloric acid, using the zinc amalgam-platinum cell previously described. The hydrogen evolved was passed through glass wool to remove spray and thence over sulfur and lead acetate. No activity was detected even in runs extending for 24 hours. In this, as in the subsequent experiments, it was difficult to obtain blanks because of the hydrogen sulfide dissolved in the acid. In all cases, however, pure molecular hydrogen was bubbled through the acid for many hours, until no trace of sulfide could be detected. Then only was the nascent hydrogen produced and tested.

Since the active hydrogen is known to be very unstable, it was possible that this method of generation was too slow. A generator with heavy platinum electrodes sealed in was then used for the electrolysis of potassium hydroxide solution with a current that could be varied from 2 to 30 amperes. The tests were extended to as long as 15 hours, but in no case was any activity noted.

Finally, pure sodium amalgam was dropped into water, and the resulting hydrogen was tested as before. Again there was no activity.

The failure of these experiments does not necessarily exclude the mechanism of formation advanced. We are here between two experimental difficulties. The hydrogen must be evolved so rapidly that it reaches the sulfur within one minute, to avoid the decomposition of the active form into the ordinary. On the other hand, if evolution is made rapid, the gas carries with it large amounts of spray which are practically impossible to remove without slowing up the stream of gas more than can be allowed. The one possible means would be electrical precipitation of the droplets, but that was excluded because the electrical discharge itself would activate the hydrogen. Hence the sulfur may well have become coated with a film of moisture which prevented the access of the active hydrogen.

### Catalytic Decomposition

During the course of the work it was invariably found that the active hydrogen could not be produced in copper or brass tubes and that there is a peculiar fatigue effect even when glass tubes are used. To determine the presence of catalytic decomposition such as is very common in the case of ozone itself, the hydrogen was therefore activated in the Siemens glass tube ozonizer, and was passed through a tube containing finely divided metals. No tests for activity could be obtained when the following metals were used: platinum, nickel, copper, lead, antimony and cadmium. There was, however, no destruction of the activity by silver, mercury, tin, bismuth, molybdenum, zinc or aluminum. The catalytic decomposition by

copper therefore explains the failure of brass tubes to give the active gas. The fatigue effect seems to be due to the formation of finely divided platinum on the walls of the discharge tubes by spluttering from the electrodes during the passage of the current. Whenever the tubes showed fatigue they could be restored to their original activating power by removing this film of platinum, though all other efforts, such as renewing the sulfur, had no effect. The fatigue effect was never observed when the glass ozonizer with external electrodes was used.

### Contraction in Volume

The evidence for a triatomic structure of the active hydrogen molecule was summarized in the previous paper. It is difficult to establish the contraction which is to be expected from the activation by the electrical discharge if a polyatomic molecule is formed, because of the heat developed by the discharge. The device shown in Fig. 1, however, eliminated this interference and gave conclusive evidence of contraction.

A is the glass discharge tube with platinum electrodes, operated by a 20,000 volt Thordarson wireless transformer and using currents of 25 milli-amperes. It was im-

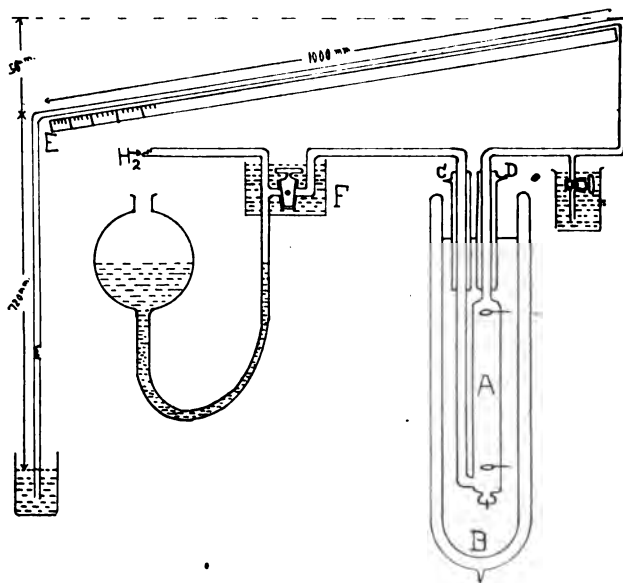


Fig. 1.

mersed in the Dewar cylinder, B, which in the various experiments contained constant temperature cooling mixtures. The tubes, C and D, cover the inlet and outlet tubes at the points where they enter the liquid. They were thoroughly evacuated before sealing and thus acted as insulators to guard against any thermal effects on the gas within from possible variation in the level of the cooling liquid in the Dewar cylinder. E is a mercury manometer the upper part of which is sloped, rising 1 cm. vertically for 20 cm. of length, in order to increase its sensitiveness. The 2 stopcocks were sealed with mercury. The

mercury level was raised above the stopcock, F, by raising the leveling bulb before the cock was closed, in order to prevent the possibility of leakage through the cock. When the tube was filled with hydrogen at 3cm. pressure and sealed, there was first an increase in pressure due to heating. Equilibrium was soon established, however, and a decrease in pressure became evident in all cases. On shutting off the current there was first a rapid, then a slower increase in pressure, until the original pressure was restored. The restoration of the original pressure proves the absence of impurities such as oxygen or nitrogen which might have reacted, and shows also the instability of the active gas. Data for typical contractions follow.

At 0°, under ice-water mixture: maximum pressure at start of contraction, 30.00 mm.; successive pressures at intervals of 10 seconds, 29.6, 29.2, 28.8, 28.65, 28.30; total contraction in 50 seconds, 1.70 mm.

At -38°, under liquid ammonia: maximum pressure, 30.00 mm.; successive pressures at intervals of 3 seconds, 29.85, 29.70, 29.55, 29.40, 29.25, 29.05, 28.90; total contraction in 21 seconds, 1.10 mm.

At -85°, under carbon dioxide snow suspended in acetone: maximum pressure, 30.00 mm.; successive pressures at intervals of 5 seconds, 29.60, 29.30, 29.10, 28.95; total contraction in 20 seconds, 10.5 mm.

At -180°, under liquid oxygen: maximum pressure 24.0 mm.; successive pressures at intervals of 5 seconds, 23.70, 22.85, 22.25, 20.65, 20.10, 19.20, 17.45, 15.80; total contraction in 40 seconds, 8.20 mm.

Total contraction reduced to 40 seconds: at 0°, 1.4 mm.; at -38°, 2.10 mm.; at -85°, 2.10 mm.; at -180°, 8.20 mm.

The amount of contraction indicated that much larger amounts of the active gas were formed than had been revealed by the dynamic methods in which a stream of the gas was passed over sulfur, amounting in some cases to more than 5%. In the chemical tests a large fraction of the active gas is evidently decomposed before it has opportunity to react with sulfur. The data are not sufficiently accurate to allow a reliable calculation of the percentage of triatomic hydrogen present, nor was equilibrium reached in any case. The method can, perhaps, be extended to such measurements. It is noteworthy, too, that the contraction increases with a decrease in temperature, as would be expected for polymerization. The figures for -180° refer to the temperature of liquid oxygen, this being used in place of liquid air because of the much greater constancy of its boiling point; it was of course essential that the temperature of the tube should not change during the test. The very large contraction in this case, amounting to more than one-third the entire volume, indicates a condensation of liquid "hyzone," as is described in the next section.

The possible extraneous effects which might invalidate the observed contraction, such as leaks, heating of the surrounding liquid, insufficient cooling, and a decrease in level of the cooling liquid, all would tend to increase the pressure and are thus inoperative for such an inexact determination of the contraction as this. The one exception is the possibility that hydrogen enters the platinum electrodes under the influence of the discharge. This is practically excluded by the exact return to the original volume. Conclusive evidence that such an effect was not inter-



fering was obtained by repeating the experiment in every detail, with the same tube and electrodes, but substituting pure helium for pure hydrogen. Helium has been shown<sup>7</sup> to be easily absorbed by the electrodes; indeed in spectroscopic work especial precautions must be taken to avoid this effect. In spite of this, however, helium showed absolutely no contraction in this test. The pressure in the tube remained at 24.5 mm. with perfect constancy for several tests, each extending for as long as 2 minutes. The actual contraction of the hydrogen by polymerization is therefore established.

### Condensation by Liquid Air

It will be noted that the above data confirm previous observations that the active hydrogen is condensed by liquid air, for the contractions in the last column amount to more than  $\frac{1}{3}$  of the entire volume present. To establish this definitely, hydrogen was now activated in the Siemens tube ozonizer immersed in liquid ammonia, which gives the greatest activation we have been able to obtain, and passed through a long coil immersed in the same 4 cooling liquids used above. The first 3 allowed the active gas to pass through unimpaired, but when liquid air was used, no trace of activity could be detected. On removal of the liquid air cylinder, however, there was an immediate and rapid evolution of the "hyzone," if so it may be called. The test paper was blackened within a few seconds. This therefore establishes definitely the condensation of this gas at a temperature of  $-180^{\circ}$ . There had previously been some question as to whether its removal at that temperature was due to rapid decomposition by adsorption on the walls at the low temperature, but there is now no doubt that the hyzone has a true boiling point above that of liquid air. It was not possible, however, to collect sufficient quantities of the liquid to render it visible as such.

### Spectral Evidence

The theoretical importance of the spectrum of hydrogen has led to many investigations of it. In almost all these, light emission was produced by electrical excitation. Hence in those cases the ozone form must always have been present. To select the lines due to triatomic hydrogen, we therefore planned to measure its absorption spectrum by means of a brass tube 6 meters long and 10 cm. in diameter through the axis of which passed a platinum wire attached to the high voltage transformer. At each end was a heavy plate glass mirror, one of which was fitted with 2 quartz lens windows. Light from an uncovered Nernst glower was reflected into the tube through one window, thence back and forth through the length of the tube three times and out of the other window into the slit of a Hilger quartz spectrograph. Hydrogen was passed continuously

<sup>7</sup> Soddy and Mackenzie, *Proc. Roy. Soc. (London)*, 80, 92 (1897).

through the tube at a rapid rate. The high potential discharge was turned on for a minute, and then cut off while the light from the glower passed through the tube. These alternations were repeated for many minutes. In no case was any absorption noted. This may have been due to the catalytic decomposition of the hyzone by the brass walls of the tube, though no better results were obtained when the inner wall was coated with graphite.

In another connection, however, spectral evidence was obtained. During the experiments on the contraction in volume at liquid-air temperatures, the color of the discharge went through interesting changes. Beginning with the usual lavender color, an intensification of the red first appeared. For a half-minute the color was brick red, then shifted rapidly through orange to yellow, and remained finally at a bright, greenish yellow, practically straw-color. Examination with a visual spectroscope showed the few series lines of hydrogen still present, though much weakened, and a brilliant display of the secondary line spectrum. This effect of liquid air has been observed by Lemon,<sup>8</sup> though his secondary spectrum extended from the red  $H_{\alpha}$  line only about half-way to the green line. We observed the lines, appearing much like fluted bands, well into the green. This may have been due to our use of much heavier currents, up to 25 milli-amperes. The intensification of the secondary line spectrum is usually attributed to polymerization, such as the formation of hyzone in this case. The fact that, though the hydrogen is well cooled before the discharge passes, the appearance of the secondary spectrum is a slow and progressive process, is in accord with the assumption that the heavier molecules are concerned and do not show their effect until the current has had time to produce them. If the current is shut off for a few minutes, the color on exciting the gas once more is yellow at once, as would be expected from the condensation of the hyzone at this temperature. Lemon's experimental apparatus was not so mounted that he could observe the growth of color visually.

### Mechanism of Formation

Nothing has occurred since the publication of the previous paper to invalidate the explanation of the mechanism of formation of hyzone there suggested, with the exception of the failure to show a transitory active state in hydrogen collected from electrolysis or the solution of metals. This failure, however, is inconclusive in this regard.

A. L. Hughes,<sup>9</sup> however, has studied the clean-up of hydrogen at pressures of  $10^{-3}$  mm. by electrons projected from a hot filament under voltages of above 13 volts and finds, as Langmuir<sup>10</sup> did, that the greater part of the

<sup>8</sup> Lemon, *Astrophys. J.*, 35, 109-124 (1912).

<sup>9</sup> Hughes, *Phil. Mag.*, 41, 778 (1921).

<sup>10</sup> Langmuir, *THIS JOURNAL*, 37, 451 (1915).

hydrogen ceases to exert pressure, being condensed on the glass walls which are immersed in liquid air. On removing the liquid air, the gas is regenerated, and thereafter only a part of it can be recondensed. This he attributes to a formation of atomic hydrogen by the electron collisions and a condensation of the atoms on the glass walls. When the temperature is raised, the atoms combine to form molecules, and only those remaining in the atomic form are recondensed. Thus ionization by electrons, at least by those with energies above 13 volts, is accompanied by atomization, as had been suggested by Franck, Knipping and Krüger<sup>11</sup> and as we assumed in the previous paper. While the condensation observed by Langmuir and by Hughes may at the low pressures used have been chiefly that of atomic hydrogen, at the higher pressures used in our experiments, where the mean free path of a molecule is much less than the diameter of the tube, the formation of hyzone is more probable, and even in the former work may have exerted a greater influence than was suspected. In any case, atomization accompanies ionization and furnishes the most probable explanation of the formation of the active modification of hydrogen. Atomization may be assumed also in Venkataramaiah's explosion method for the preparation of this gas.

### The Molecular Formula

All the evidence now presented favors the view that this new gas has a larger molecule than  $H_2$ , including its reactivity, its relative stability at atmospheric pressure, its condensation by liquid air, its catalytic decomposition by metals, its contraction on formation, and its effect on the spectrum. Positive-ray analysis indicates a triatomic molecule.

The one alternative possibility, however, has been accepted by Baly,<sup>12</sup> namely that it is the isotope of hydrogen suggested by Harkins<sup>13</sup> as the basis of the structure of many heavier atoms. It is unfortunate that Harkins' use of the symbol  $H_3$  for that isotope has led to some confusion. The ozone form of hydrogen may, of course, properly be designated as  $H_3$ , which represents 3 separate hydrogen atoms combined into one molecule. The isotope, which we shall refer to as iso-hydrogen, however, is a single atom with an atomic weight of 3 units. Like hydrogen itself, it has but a single free electron, and should be similar to, if not identical with, hydrogen in all its chemical properties. Its nucleus consists of a compact of 3 ordinary hydrogen nuclei held together by two cementing electrons. Baly, then, refers to our preparation of the true  $H_3$  as demonstrating the existence of Harkins' iso-hydrogen and thus confirming the correctness of Harkins' fascinating hypotheses of the nuclear structure of atoms.

<sup>11</sup> Franck, Knipping and Krüger, *Verh. Deut. Physik. Ges.*, **21**, 728 (1919).

<sup>12</sup> Baly, "Annual Reports of the Progress of Chemistry," Chemical Society, London, 1920.

<sup>13</sup> Harkins, *Phys. Rev.*, **15**, 73 (1920).

To this view we cannot subscribe. More proof is needed before the actual preparation of one atomic species from another is demonstrated, especially before we can believe that a heavier nucleus has been built up from lighter ones. But *a priori* nothing should be judged impossible, and it is well to review the evidence.

There are, in fact, only two sound arguments against such an interpretation. One is the almost insuperable one that very large amounts of energy should be required to condense 3 positive nuclei and 2 negative electrons into one dense and coherent nucleus; in such gentle methods of preparation as the use of the hot wire, for instance, such amounts of energy were certainly not available. The second is that the iso-hydrogen should in the gaseous state have a diatomic molecule and hence a molecular weight of 6. But positive ray spectrographs fail to show any trace of molecules of such weight.

On the other hand, numerous facts established are wholly compatible with the assumption that iso-hydrogen is present. The high reactivity of the new gas might be thought to exclude iso-hydrogen, since isotopes have been in all cases shown to be chemically inseparable and identical. This may be true, however, for differences of a few units in an atomic weight of 208, as in the case of lead, and yet not pertain to a tripling of the atomic weight as would be the case here. Furthermore, if there were a difference, the iso-hydrogen should be more reactive than the ordinary form. Its nucleus is complex and contains two negative electrons; the net positive charge of one cannot be as concentrated as it is in hydrogen itself, and might therefore hold the planetary electron less firmly than does the single positive nucleus. The fact of increased reactivity is, therefore, not wholly incompatible with Baly's interpretation. Neither does the spectral evidence exclude the latter. The spectrum of iso-hydrogen may well be more complex than the usual one, although the marked change from the simple line spectrum to the highly complex and extended secondary spectrum observed is not to be expected. A coincidence of the spectrum of iso-hydrogen with that of the hypothetical nebular element nebulium is rather more probable. Finally, the observed contraction in volume is also no criterion, since the formation of iso-hydrogen would result in a marked contraction by the reaction  $3\text{H}_2 = \text{Iso-H}_2$ . The volume would thus be reduced to one-third. A quantitative study of the contraction would therefore furnish a critical test, but no technique for it has yet been developed.

There remain two facts which favor the iso-hydrogen interpretation. The first is inconclusive, namely, the fact that we were unable to obtain evidence for transitory activity in the hydrogen collected from electrolysis or the solution of metals in acid. No activity would be expected in case we have been dealing with iso-hydrogen, for the mere contact of single atoms

of nascent hydrogen would certainly not suffice to combine them into new atomic species. But, as stated above, this negative evidence is open to question. We come at last to the high boiling point of the new hydrogen. This is certainly above the boiling point of liquid oxygen, and therefore at least  $70^{\circ}$  above the boiling point of hydrogen itself. The difference in boiling points of oxygen and ozone is only  $62^{\circ}$ . On the absolute scale the boiling points of oxygen and ozone are  $90^{\circ}$  and  $152^{\circ}$ , while those of hydrogen and of hyzone are  $20^{\circ}$  and above  $90^{\circ}$ . This is an unexpectedly large difference, especially since the boiling point of hyzone may be far above  $90^{\circ}$ , though not higher than  $190^{\circ}$ . On the other hand, it would not be so strange, perhaps, if iso-hydrogen had a relatively high boiling point and low vapor pressure, since its molecule is three times as heavy as that of ordinary hydrogen.

In view of this evidence, then, it is preferable to assume the formation of triatomic molecules, and to consider atomic transmutation as yet un-effected.

### Summary

1. Triatomic hydrogen has now been prepared by three new methods: the Siemens glass tube ozonizer, the high frequency Tesla discharge, and thermionic emission. Attempts to show its presence in hydrogen produced as nascent hydrogen from solutions of hydrogen ions were unsuccessful.

2. This hydrogen is catalytically decomposed by finely divided platinum, nickel, copper, lead, antimony and cadmium. It is not affected by contact with silver, mercury, tin, bismuth, molybdenum, zinc or aluminum.

3. Contraction in volume occurs when this hydrogen is produced by the electrical discharge at a pressure of 3 cm. This is particularly marked at the temperatures of liquid ammonia and of solid carbon dioxide.

4. This hydrogen is condensed to the liquid form by exposure to the temperature of liquid oxygen.

5. The spectrum of hydrogen at the temperature of liquid oxygen shows a progressive intensification of the secondary line spectrum at the expense of the primary series spectrum, which is probably due to the gradual formation of this triatomic form.

6. The effect of this work and that of others is held to confirm the mechanism of formation previously advanced.

7. The formula of the new gas is probably  $H_3$ , and not iso- $H_3$ , an atomic species proposed by Harkins as a constituent of heavier atoms.

8. We gratefully acknowledge our indebtedness to the Bureau of Engineering, U. S. Navy Department for the gift of a cylinder of helium gas;

to the Director of the Ryerson Physical Laboratory of the University of Chicago for the use of indispensable apparatus and instruments; and especially to E. I. DuPont de Nemours and Co. for the establishment of a research fellowship under the tenancy of which by one of us much of this work was done.

CHICAGO, ILLINOIS

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## CLAY AS AN AMPHOLYTE

BY OLOF ARRHENIUS

Received November 28, 1921

Most soil scientists know that alkali soils during filtration cause serious troubles, because the extract is grayish or turbid. Furthermore, it is a well known fact that alkali stabilizes, whereas acid peptizes the soil suspensions.

The rate of settling of soil suspensions plays a great role in mechanical soil analysis, and there has been much discussion on this subject, such as that between Rohland<sup>1</sup> and Maschhaupt,<sup>2</sup> in which the divergences were great and both were right. Rohland points out that the same addition of alkali or acid does not cause the same effect in suspensions of different soils and Maschhaupt finds that alkali first stabilizes and then suddenly peptizes the suspensions.

It is very probable that the actual acidity of the suspension, the hydrogen-ion concentration, plays the greatest role, rather than the amount of acid or alkali added. From this point of view it is not astonishing that the authors mentioned above and several others have not been able to find a satisfactory explanation. The conception of the soil as a buffer is a rather recent one,<sup>3,4</sup> but only when one assumes this buffer action is one able to understand why some soils change their reaction markedly and others not at all when the same amount of acid is added to each.

In order to ascertain the influence of the hydrogen-ion concentration and compare it with that of the amounts of alkali and acid added, the following experiment was carried out.

Two clay soils, one used for brick-making, with a Sørensen value ( $P_H$ ) of 7.5 and another, a peaty clay with a Sørensen value of 5.0, were used for making up the suspensions. Two hundred and fifty cc. portions of each suspension (100 g. of clay in 5 liters of water) were placed in glass cylinders; alkali or acid was then added and the different lots filled up to the same volume, 350 cc. The suspensions were then shaken and left

<sup>1</sup> Rohland, *Landw. Vers. Sta.*, 1914, 85.

<sup>2</sup> Maschhaupt, *ibid.*, 1914, 83.

<sup>3</sup> Bjerrum, *Landbo og Veterinaerhøisk. Aarskr.*, 1917.

<sup>4</sup> Arrhenius, *Soil Science*, 1922.

to settle. After definite intervals of time, the heights of the clear columns were measured. The data thus obtained are shown in the table below.

TABLE I

Brick Clay				Peaty Clay	
Cc. of acid	Cc. of alkali	Sörensen value	Settling rate cc./hour	Sörensen value	Settling rate cc./hour
100 (HCl)	...	...	...	0.5	3.0
20	...	2.5	38	...	...
10	...	...	...	2.5	2.5
9	...	...	...	2.7	2.0
8	...	...	...	3.1	1.5
7	...	...	...	3.4	0.5
6	...	3.8	25	3.8	0.5
5.5	...	4.0	33	...	...
5	...	4.2	38	4.0	0.5
4.5	...	4.3	48	...	...
4	...	4.5	39	...	...
3.5	...	4.9	36	...	...
2	...	6.2	13	4.2	1.0
1	...	...	...	4.3	2.0
0.5	...	...	...	4.5	1.0
0	0	7.5	0.3	5.0	0.1
...	4.5	8.4	0.1	6.7	0.05
...	9	10	0.001	7.5	0.01
...	11	11	0.1	...	...
...	13.5	12	1.4	...	...
...	18	...	...	8.4	0.001
...	27	12.5	25	...	...
...	40	...	...	9	0
...	90	...	...	11	0.5
...	140	...	...	12	2.0

With the data given in this table the curves have been constructed. It is easily seen that the curves are very similar. Beginning on the acid side there is a decrease in the rate of settling and the curve sharply bends over into an increasing branch till the iso-electric point is reached (the maximum rate). Then, with lower hydrogen-ion concentration the suspension is more and more stabilized and thus the settling rate reaches a minimum, after which at high alkalinity the rate increases decidedly again.

Wilson and Heisig<sup>5</sup> found the same type of curve as far as their experiments went for sewage sludge when measuring the influence of hydrogen-ion concentration on the rate of filtration.

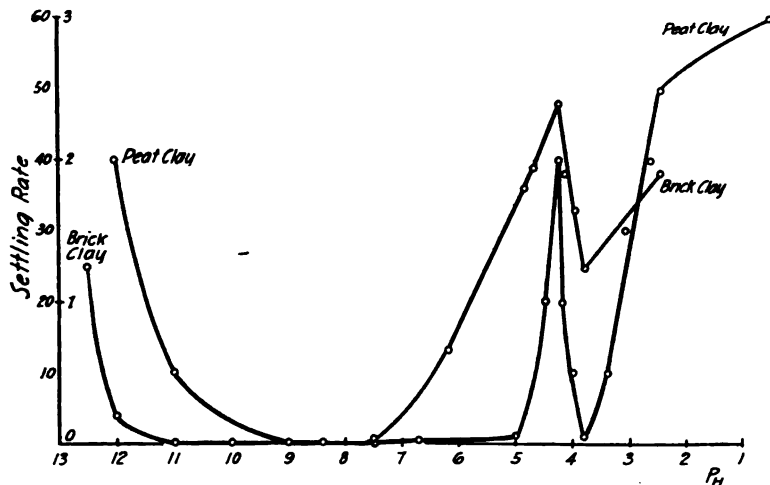
It is interesting that this curve is almost the same as that for the swelling of gelatin, showing that the clay acts as an ampholyte just as does gelatin,

<sup>5</sup> Wilson and Heisig, *J. Ind. Eng. Chem.*, 13, 406 (1921).

and therefore the course of the curve may be explained by the help of the Donnan equilibrium as shown in Loeb's interesting experiments.<sup>6</sup>

If the clay indeed acts as an ampholyte, it should combine stoichiometrically with acids and bases as shown by Loeb. This is actually the case. When using sulfuric acid the rate of settling is double that when using phosphoric acid, hydrochloric or oxalic acid, which is in full agreement with Loeb's investigations.

Another proof of this theory is drawn from Rohland's<sup>1</sup> paper. He mentions that it is impossible to compare the adsorption of different dyes caused by soils, because they are adsorbed to different extents. He points



out that Vesuvium solution is decolorized by about 15 g. of clay, three times as much as required by an equal amount of Victoria blue. Beilstein's "Handbuch" gives the molecular weight of Vesuvium as 227, whereas Victoria blue has that of 505. The ratio between these two is 2.0, which is quite near the ratio given above, considering the big errors involved in these experiments. The author has found in some preliminary experiments that indicators are "adsorbed" by the same clay in proportion to their molecular weight. Whitney and Ober<sup>7</sup> found that colloidal arsenic trioxide when precipitated with calcium, strontium or barium chloride "adsorbed" 39, 77 and 152 parts of the cations as compared with the atomic weights 40, 88 and 137.

Thus Loeb's assumption that ampholytes combine with acids or bases in stoichiometrical proportions holds also for the mineral ampholytes of the soil. The facts here shown may have a revolutionary effect on our conception of the soil and the soil conditions. We may dispense with such

<sup>6</sup> Loeb, *J. Gen. Physiol.*, 1920, 1921.

<sup>7</sup> Whitney and Ober, *Z. physik. Chem.*, 41, 379 (1902).



convenient words as adsorption used by the colloid chemists, since we see that purely physico-chemical laws find application to mineral colloids also, in this case the soil. The word colloid will then mean only a particle of special dimensions and not of special properties.

### Summary

It has been shown that clays of different origin and different reaction have the same iso-electric point and the curve obtained by plotting rate of settling against the hydrogen-ion concentration has the same course as that of gelatin. The clay acts as an amphoteric electrolyte and can therefore combine with either acid or base. This is also shown by the buffer action of the clays. The result is important theoretically, as well as practically.

The work has been carried out in the Laboratory of Plant Physiology of Harvard University. To Professor Osterhout I express my warmest thanks for his kind help and suggestions.

STOCKHOLM, SWEDEN

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[CONTRIBUTION FROM THE WOLCOTT GIBBS MEMORIAL LABORATORY, HARVARD UNIVERSITY]

## SOLID THALLIUM AMALGAMS AND THE ELECTRODE POTENTIAL OF PURE THALLIUM

BY THEODORE W. RICHARDS AND CHARLES P. SMYTH

Received December 1, 1921

This investigation was undertaken for the purpose of ascertaining the cause of the potential difference recently found to exist between pure thallium and saturated thallium amalgam. Several earlier investigators concluded that, as in the case of zinc, the solid phase in equilibrium with the liquid in the 2-phase amalgam consists of pure solid metal,—the solubility of mercury in solid thallium being regarded as practically zero, when, of course, the potential of the 2-phase amalgam would be identical with that of pure thallium. Lewis and von Ende,<sup>1</sup> in their excellent determination of the potential of the thallium electrode, assumed this to be the case, and used, in place of a pure thallium electrode, a 55% amalgam consisting of 2 phases. The basis for their assumption was the thermal analysis of Kurnakov and Puschin,<sup>2</sup> the electromotive force measurements of Sucheni,<sup>3</sup> and experiments of their own.

The experimental precautions employed, however, were evidently not adequate to prove the point, for the work of recent Harvard investigators

<sup>1</sup> Lewis and von Ende, *THIS JOURNAL*, 32, 732 (1910).

<sup>2</sup> Kurnakov and Puschin, *Z. anorg. Chem.*, 30, 86 (1902).

<sup>3</sup> Sucheni, *Z. Elektrochem.*, 12, 726 (1906). See also Spencer, *ibid.*, 11, 681 (1905).

has shown a real difference of electromotive force between pure thallium and thallium with a film of amalgam on its surface.<sup>4</sup>

The main objects of the present investigation were to confirm this difference of potential as well as to discover whether it is due to the formation of a solid solution of mercury and thallium, or to a crystalline compound. Incidentally, the electrode potential of thallium was revised.

### Experimental Details

The substances used were purified with adequate care: the water was twice distilled (from alkaline permanganate and very dil. sulfuric acid); hydrogen was generated electrolytically (from sodium hydroxide containing a little barium hydroxide) and thoroughly dried; and mercury was purified by treatment with mercurous nitrate solution and distillation. The preparation of the pure thallium must be described more in detail. This was chiefly at hand in the form of nuggets of crude metal containing perhaps 7% of lead and small amounts of other impurities. The thallium was dissolved in dil. pure sulfuric acid, leaving most of the lead, partly as a metallic powder and partly as precipitated sulfate. The cooled and somewhat diluted solution was filtered; to it was added dil. redistilled hydrochloric acid drop by drop, with constant stirring. Very little, if any, lead was found in the precipitated thallous chloride, which was washed several times by decantation. Pure conc. redistilled sulfuric acid converted the solid thallous chloride into sulfate. This thallium sulfate, which on dilution gave no precipitate of lead sulfate, was crystallized by cooling to 0°. The long needles of the salt were thoroughly dried, recrystallized at least twice (sometimes thrice) in a silica dish, by cooling with ice a solution almost saturated at the boiling point. The solubility curve is steep and the process efficient.

From this sulfate, which must have been amply pure enough for our purpose, metallic thallium was prepared by the electrolysis of the saturated solution of the sulfate in water; the electrodes were short platinum wires exposing not more than 1 cm. of their length to the solution. The anode was placed on the bottom of the beaker containing the solution (being protected above by a long glass tube into which it was sealed), while the cathode merely dipped beneath the surface. The heavy red-brown deposit of peroxide at the anode remained at the bottom of the beaker and therefore did not contaminate the crystalline spongy mass of thallium deposited on the cathode above. A current of about 1 ampere was used and the thallium was removed at frequent intervals from the cathode by means of a small glass fork, rinsed thoroughly with pure water, pressed together, and kept under pure boiled water until fused. A small further amount of thallium was obtained by electrolysis from pure liquid amalgam remaining from the work of Daniels, the amalgam being made the anode in dil. sulfuric acid solution. This thallium was found to contain traces of mercury, which were removed by fusing at a high temperature.

For use in the study of the amalgams, as well as of the pure metal, the thallium was fused into a compact mass. The sponge was pressed as free from water as possible, and dried in a vacuum desiccator. At first the dried thallium was pressed into one of three Pyrex glass bulbs connected by capillary tubes. After sealing and thorough evacuation of the tube, the thallium was melted; and, by tilting the apparatus, the molten metal was run through the capillary into the second bulb, leaving the solid impurities behind. The clean, bright metal was then heated to drive off volatile im-

<sup>4</sup> Richards and Daniels, *THIS JOURNAL*, 41, 1732 (1919). Jones and Schumb, *Proc. Am. Acad.*, 56, 199 (1921). See also Lewis and Randall, *THIS JOURNAL*, 43, 247 (1921) (Footnote).

purities (if any) into the third bulb; after which the apparatus was sealed off between the second and third bulbs, leaving the pure metal in the second bulb. Here it could be kept indefinitely without fear of oxidation.

Later, with larger quantities of metal, another less elegant but more convenient technique was employed. The dried sponge was pressed into a large unglazed earthenware boat, which was slipped into the glazed porcelain tube of an electric furnace. The tube, wound with resistance ribbon and asbestos, was supported in a horizontal position by large clamps, and its ends were closed tightly with Hempel stoppers, through which constant streams of cold water were kept flowing. Air was at once removed by an oil pump and replaced by hydrogen, the exhaustion and replacement by hydrogen being repeated thrice. All heating was conducted in an atmosphere of hydrogen, which was kept flowing through the tube in a slow, but steady, stream. A temperature between 350° and 400° was maintained from 1 to 3 hours. Most of the oxide present was reduced to the metal, and volatile impurities were driven off. Usually a very thin scarcely weighable grayish coating of non-metallic impurities remained upon the surface of the compact ingot of pure metal, which was scraped clean and bright before using.

The same technique was adequate for the removal of mercury from very concentrated amalgams. When much mercury was evaporated, it was found to carry with it a trace of thallium,<sup>5</sup> so that the method is not a very good one for purposes of analysis, but the residual thallium appeared to be beyond reproach. In order to make certain of the expulsion of every trace of mercury, the ingot was reheated at least once in hydrogen after cleansing the furnace.

From this pure thallium, amalgams were prepared as follows. The desired amount of solid metal was scraped until thoroughly clean, weighed, and mixed with a weighed quantity of mercury. The amalgamation was at first effected by heat in a sealed glass tube, but the method had disadvantages and was abandoned in favor of a simpler one in which the mercury and thallium were brought together in a small porcelain crucible and immediately covered with molten paraffin, with which the crucible was almost filled. Gentle heating melted the thallium, and the metals were stirred together with a fine glass rod until they formed a homogeneous liquid amalgam. This was allowed to cool slowly. The layer of paraffin above the amalgam prevented oxidation of the thallium, and evaporation of mercury, and served also to render cooling more uniform, and to protect the bead of amalgam from air until needed. The solid bead after cleaning free from paraffin, showed a bright, clean surface.

The amalgams were analyzed by a method already described,<sup>6</sup> enough mercury being added to the solid amalgam to effect its solution, and the liquid being agitated with pure air and standard dil. acid. The method was tested by two preliminary determinations made with pure thallium in the same fashion. Thus 0.1309 g. of metal was estimated as 0.1307 g. and 0.2200 g. as 0.2201 g., indicating adequate precision.

Thallium is deposited electrolytically in hexagonal plates.<sup>7</sup> Whether or not these belong to the hexagonal system we did not decide. Solid amalgams containing over 10% of mercury were quite different in appearance and properties from the pure metal. When less than 10% of mercury was present, they could be cut smoothly with a knife, but amalgams with more mercury, especially those containing 12%, were distinctly brittle, breaking up into grains which appeared to be well formed cubic, or near-cubic,

<sup>5</sup> Compare Krafft and Knocke, *Ber.*, 42, 202 (1909), and von Wartenberg, *Z. Elektrochem.*, 19, 482 (1913).

<sup>6</sup> Richards and Daniels, *THIS JOURNAL*, 41, 1732 (1919).

<sup>7</sup> Our observations on this matter agree with Kurnakov and Puschin, *Z. anorg. Chem.*, 52, 430 (1907).

crystals. This implies the formation of a new solid phase, the nature of which will receive discussion later. When more than 12% of mercury was present, a trace of liquid amalgam was sometimes found on the faces of the freshly formed crystals. On standing, this excess of mercury seemed to have incorporated itself into the amalgam as solid. It must be remembered that these preparations had been solidified by cooling and that therefore the first formed crystals, when they actually separated, were in equilibrium with the liquid at a higher temperature than that of the room. Evidently thallium takes in more mercury in the solid form at a low temperature than at a high temperature; but an 85% amalgam (containing 15% by weight of mercury) contained between the solid crystals a permanent very thin layer which was not absorbed on standing. Of course, amalgams yet poorer in thallium contain still more of this liquid film. The crystals of the amalgam just mentioned are much harder than pure thallium. The pure metal is so soft that no considerable strain can exist in it at ordinary temperatures.

As regards microstructure, no satisfactory evidence could be obtained by polishing and etching the surfaces, for, of course, the mercury set free at once covered the surface with a shining layer of liquid amalgam. On solidifying, the solid amalgams showed delicate fern-like patterns on their surfaces, but these gave no evidence of the crystalline structure.

### The Electromotive Force between Amalgams

The measurements of electromotive force were made by the usual Poggendorff compensation method, a Wolff potentiometer and a highly sensitive galvanometer being used. The potentiometer was standardized by a Weston cell certified by the Bureau of Standards. All usual precautions were taken for obtaining results of high accuracy. The thallium cells were kept at 20.00° in an electrically regulated thermostat (with a cooling coil for hot weather). They were contained in vessels of the ordinary H type, the electrical connections being made through short platinum wires sealed into fine straight tubes which passed through paraffined corks. The electrolyte was at first a saturated solution of thallium sulfate with crystals of the salt in each arm, but afterwards a dilute solution was found to be more convenient, since the changes of temperature in the cells after removal from the thermostat caused changes of concentration when solid sulfate was present, which were slow in equalizing themselves. The most convenient standard of reference for all the thallium amalgams was the 2-phase amalgam containing 55% of thallium and 45% of mercury, as recommended by Lewis and von Ende. This is a very constant and reproducible electrode. A portion of 2-phase amalgam thus prepared was always placed in one arm of each H-cell; in the other arm was placed one of the various amalgams to be studied. Twenty or more cells were thus equipped at one time, and 76 in all were measured.

Electrodes of electrolytic thallium were prepared by electro-deposition from a thallic sulfate solution in several ways, the deposit being made upon a short platinum wire. The ordinary procedure was to use a very low current for an hour or two until the wire was well covered with a compact deposit of thallium, after which the current was increased so that a spongy deposit with a large surface formed rapidly. A few electrodes were prepared by running a very low current for 2 or 3 days, the small deposit thus obtained being very thin, adherent, and finely crystalline.

Electrodes were prepared also from pieces of the thallium which had been fused in hydrogen. The piece which, usually, had a maximum cross-sectional area of about 0.5 sq. cm., was cut with a knife, and into the deep slit thus formed the short platinum wire of a connecting tube was forced, the metal was pressed together over the wire, and a little paraffin was melted over the closed slit and over any exposed portion of the platinum wire. Connection with the electrode was thus made in such a manner

that the thallous sulfate solution in the cell could have no access to any metal other than that of the electrode. All the electrodes were rinsed several times with thallous sulfate solution before use in the cell. Solid thallium amalgams were mounted as electrodes in the way just described.

In all except the very first experiments, considerable precaution was taken against the presence of oxygen in the electrolyte above the amalgams, the gas above the liquid being repeatedly exhausted and replaced by pure hydrogen before the electrode to be studied was introduced, and this introduction was effected while the hydrogen was flowing in a rapid stream. In the first few cells only was there any considerable oxidation. The electromotive forces usually remain constant for a long time. This constancy was evidence also that mercury was not appreciably transferred from the 55% amalgam to the other electrode during the time of experimentation. In a few cases the electrolyte was found, after a long time, to have become alkaline to phenolphthalein, but what little alkalinity existed was equally distributed through the cell so as not to affect the electromotive force, which depends not upon the character of the electrolyte, if uniform, but upon the concentration in thallium of the two electrodes.

Preliminary measurements gave fairly constant results for spongy, electrolytically deposited thallium, varying from 2.60 to 2.81 millivolts when compared with the 2-phase 55% amalgam. Fused thallium gave 2.08 mv. Solid amalgams containing between 85 and 100% of thallium all gave lower results, as had been expected. The final values obtained (the averages of many measurements) are given in the following table. The individual determinations rarely differed more than 0.10 mv. from the average in the case of the most significant figures between 96 and 91%, the reproducibility of the electrodes increasing with increasing mercury content.

TABLE I  
ELECTROMOTIVE FORCE

Pure thallium or solid amalgams versus saturated amalgam								
Negative electrode	Tl %	E.m.f. Mv.	Negative electrode	Tl %	E.m.f. Mv.	Negative electrode	Tl %	E.m.f. Mv.
Elec. deposit (fresh): pure Tl	100	2.67						
Fused: pure Tl	100	2.08	Fused amalgam	95	1.32	Fused amalgam	89	1.02
	99	1.80		94	1.39		88	0.59
	97	1.47		93	1.26		87	0.39
	96	1.28		91	1.30		86	0.15
Fused amalgam				90	1.10		85	0.00

Let us consider first the behavior of the pure metal under different conditions. Electrolytically deposited thallium gave, when freshly prepared, a potential 0.6 mv. higher than that of thallium which had been fused—a difference seemingly too great to be accounted for on the ground of experimental error, since the lowest individual determination for fresh spongy, electrolytic thallium was higher than the highest individual determination for the compact form.

This difference might be ascribed to one or more of three different possible causes. It might be due to active hydrogen, released at the cath-

ode along with the metal during the electrolysis. Although thallium occludes ordinary gaseous hydrogen in quantities which can hardly be detected,<sup>8</sup> possibly hydrogen formed at a cathode during electrolysis might be occluded to a greater extent, as in the case of iron.<sup>9</sup> Accordingly, qualitative experiments were made to test the point. The samples to be tested were dissolved in mercury under water in a test-tube to form a dil. amalgam, in which hydrogen must have been practically insoluble. Fused thallium evolved no gas when thus treated, nor did electrolytic thallium which had been long prepared. Freshly made electrolytic thallium evolved a few bubbles, but unfortunately the results of this latter test were inconclusive, as they could not show whether the hydrogen was actually occluded in the metal, or merely held on its surface, or in cavities. At any rate the total amount of hydrogen was shown to be very small.

Another possible explanation for the difference of potential between fused and electrolytic thallium lies in the allotropy of the metal. When a metal capable of existing in more than one form is deposited electrolytically, the metastable form is likely to be deposited first.<sup>10</sup> This metastable form may change rapidly to the modification which is stable under the existing conditions, or may remain unchanged for a longer period of time. The metastable form has, of course, a higher potential than the stable.<sup>11</sup> Thallium has been known for some time to exist in two enantiotropic modifications,  $\alpha$ -thallium, the form stable at ordinary temperatures, changing to  $\beta$ -thallium at the transition temperature 235.3° (as described later); but  $\beta$ -thallium has never been observed at room temperatures. An attempt was made to obtain it by quenching the liquid metal, but the attempt was a failure, since the quenched metal showed the same potential as ordinary fused thallium and was therefore the  $\alpha$  modification. There is a remote possibility that electrolytic thallium may be a hitherto undiscovered modification lying between the  $\alpha$  and the  $\beta$  forms, but the lack of any thermal evidence of its existence, and the fact that X-ray photographs of sections of the metal taken at different temperatures show no change of structure below 227°,<sup>12</sup> seem to render this possibility so remote as to deserve no serious consideration.<sup>13</sup> Complete knowledge of the

<sup>8</sup> Sieverts, *Z. Elektrochem.*, **16**, 708 (1910). Smith, *J. Phys. Chem.*, **23**, 186 (1919).

<sup>9</sup> Cailletet, *Compt. rend.*, **80**, 319 (1875). Johnson, *Proc. Roy. Soc. (London)*, **23**, 168 (1875). Bellati and Lussana, *Z. physik. Chem.*, **7**, 229 (1891). Shields, *Chem. News*, **65**, 195 (1892).

See also Richards and Behr, "The Electromotive Force of Iron under Varying Conditions, and the Effect of Occluded Hydrogen," *Carnegie Inst. Pub.*, **61** (1906).

<sup>10</sup> Smits, *Verslag. akad. Wetenschappen Amsterdam*, **22**, 642 (1913).

<sup>11</sup> Cohen, *Trans. Faraday Soc.*, **10**, 216 (1915).

<sup>12</sup> Nishikawa and Asahara, *Phys. Rev.*, **15**, 38 (1920).

<sup>13</sup> Werigin, Lewkojeff, and Tammann (*Drude's Ann.*, **10**, 647 (1903)), measuring the change with temperature of the "Ausflussgeschwindigkeit" of thallium thought that a transformation was indicated at 180°, but other investigators have been unable to discover any such transformation.

different crystal structures of thallium might make it possible to decide conclusively against the assumption that the higher potential of the electrolytic metal is due to metastability,<sup>14</sup> but at present this explanation seems unlikely.

A more probable explanation than either of these, is that the difference of potential between the compact and finely divided thallium is due to the degree of subdivision. This effect has long been well-known in other cases: the solution tension of a fine powder is greater than that of a flat surface.<sup>15</sup> The differences in potential ascribed to this cause, as found by others in various cases, have varied from a few tenths of a millivolt to several millivolts. The small difference of 0.6 mv. found by us may well be thus produced; the gradual elimination of the finest shreds of thallium on standing would be expected to reduce the potential to the normal value.

Clearly, since the 55% amalgam lacks 2.08 mv. of the true thallium potential, the true potential for the cell [Tl, (Tl<sup>+</sup> normal), calomel electrode] at 25° is 0.6192 instead of 0.6170.<sup>16</sup> The "single electrode potential" of thallium may be taken as about 0.055 with this concentrated solution,<sup>17</sup> or about 0.115 with a Tl<sup>+</sup> 0.1 *N* solution, neglecting the junction potential of the liquids (which may, however, be fairly large).

Turning now to the amalgams of thallium, we find that the e.m.f. determinations range themselves in a broken curve of definite character. With increasing concentration of mercury there is a decrease in the potential as far as 4% or 5%, then a fairly constant potential (within a reasonable limit of error) as far as 9%, and then a rapid falling off down to 14.5%, where the potential becomes that of the 2-phase amalgam. The cause of the striking double break in this curve will be considered after other phenomena have been studied. The curve furnishes further evidence that thallium which has been fused contains no atomic hydrogen, for otherwise its e.m.f. would lie above the extrapolation of the left hand end of the curve to the vertical axis. It likewise conclusively proves

<sup>14</sup> As the crystal structure of thallium is now under investigation by A. W. Hull, who is applying to it his highly developed method of X-ray analysis, the knowledge should soon be available.

<sup>15</sup> The literature upon this subject is very plentiful. A few references are given below.

Luedtke, *Wied. Ann.*, 50, 678 (1893). Ostwald, *Z. physik. Chem.*, 34, 495 (1900). Hulett, *ibid.*, 37, 385 (1901). Richards and Behr, Ref. 9. Hering, *Met. Chem. Eng.*, 10, 14 (1912).

<sup>16</sup> Ref. 1, p. 740. Our value 0.00208 volt for this difference was at 20°; but this would be increased to about 0.00217 at 25° (See Richards and Daniels, Ref. 4, p. 1743).

<sup>17</sup> The calomel electrode is assumed to give 0.564 volt at 25° and no allowance is made for the unknown solution-junction potential.

that thallium dissolves considerable mercury in the solid state. This curve is depicted as the lowest one in Fig. 3, given later.

### Thermal Analysis of Thallium Amalgam

For amalgams containing more than 50% of mercury the melting points have been studied by one of us in collaboration with F. Daniels.<sup>18</sup> The melting point<sup>19</sup> of pure thallium has been variously given in recent years between 299.4 and 303.0 and the transition point<sup>20</sup> between the  $\alpha$  and  $\beta$  modifications of thallium variously given between 225° and 238°. In the earlier investigation only a few points had been determined with

<sup>18</sup> Ref. 4. In this paper references to earlier work of this sort will be found. See also Pavlovitch, *J. Russ. Phys. Chem. Soc.*, **47**, 29 (1915).

<sup>19</sup> Determinations of the melting-point of thallium

Melting point °C.	Observer	Publication
288	Crookes .....	<i>Phil. Mag.</i> , [4] <b>21</b> , 301 (1861)
290	Lamy .....	<i>Ann. chim. phys.</i> , [3] <b>67</b> , 385, 418
303.7	Heycock and Neville .....	<i>J. Chem. Soc.</i> , <b>65</b> , 32 (1894)
301.7	Kurnakov and Puschin .....	<i>Z. anorg. Chem.</i> , <b>30</b> , 91 (1902)
301.2	Kurnakov and Puschin .....	<i>Ibid.</i> , <b>52</b> , 430 (1907)
301	Williams .....	<i>Ibid.</i> , <b>50</b> , 127 (1906)
303	Petrenko .....	<i>Ibid.</i> , <b>50</b> , 133 (1906)
301	Chikashigé .....	<i>Ibid.</i> , <b>51</b> , 328 (1906)
302	von Vegesack .....	<i>Ibid.</i> , <b>52</b> , 30 (1907)
299.4	Lewkonja .....	<i>Ibid.</i> , <b>52</b> , 456 (1907)
301.2	Kurnakov, Zemczuzny and Tararin .....	<i>Ibid.</i> , <b>83</b> , 200 (1913)
301	Pavlovitch .....	<i>J. Russ. Phys. Chem. Soc.</i> , <b>47</b> , 29 (1915)
301.5	Roos (Electrolytic Tl) .....	<i>Z. anorg. Chem.</i> , <b>94</b> , 358 (1916)
301.7	Fuchs .....	<i>Ibid.</i> , <b>107</b> , 308 (1919).

<sup>20</sup> Determinations of the transition point of thallium

Trans. point °C.	Observer	Publication
225	Levin .....	<i>Z. anorg. Chem.</i> , <b>45</b> , 31 (1905)
226	Williams .....	<i>Ibid.</i> , <b>50</b> , 127 (1906)
227	Petrenko .....	<i>Ibid.</i> , <b>50</b> , 133 (1906)
231.6	Chikashigé .....	<i>Ibid.</i> , <b>51</b> , 328 (1906)
227	Kurnakov and Puschin .....	<i>Ibid.</i> , <b>52</b> , 430 (1907)
230.5	Lewkonja .....	<i>Ibid.</i> , <b>52</b> , 456 (1907)
234	Voss .....	<i>Ibid.</i> , <b>57</b> , 49 (1908)
238	Donski .....	<i>Ibid.</i> , <b>57</b> , 185 (1908)
229	Kurnakov, Zemczuzny and Tararin .....	<i>Ibid.</i> , <b>83</b> , 200 (1913)
226	Werner .....	<i>Ibid.</i> , <b>83</b> , 275 (1913)
234	Pavlovitch .....	<i>J. Russ. Phys. Chem. Soc.</i> , <b>47</b> , 29 (1915)
233	Roos (Electrolytic Tl) .....	<i>Z. anorg. Chem.</i> , <b>94</b> , 358 (1916)
231-233	Fuchs .....	<i>Ibid.</i> , <b>107</b> , 308 (1919)
227	Nishikawa and Asahara .....	<i>Phys. Rev.</i> , <b>15</b> , 38 (1920).



certainty on the liquidus curve for thallium-mercury mixtures containing from 80-100% of thallium. This curve therefore seemed worthy of further study. Our experiments were carried out in a large test-tube jacketed by another still larger test-tube, the thermometer being immersed in the melted metal, a stirrer being provided and carbon dioxide being led into the space above in order to protect the metal from oxidation. The outer test-tube was heated by immersion in a bath of melted sodium and potassium nitrates suitably controlled in temperature. The thermometer was calibrated in precisely the same way with pure tin certified by the U. S. Bureau of Standards and an imported pure cadmium (melting points assumed as  $231.9^{\circ}$  and  $320.7^{\circ}$  respectively).

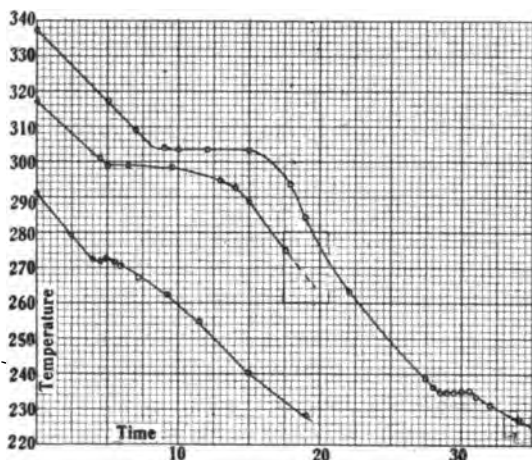


Fig. 1.—Typical cooling curves: pure thallium and two amalgams.

Temperatures are plotted as ordinates; times as abscissas. The unit of time is  $\frac{1}{2}$  minute for the uppermost curve; 1 minute for the two lower ones. The uppermost curve is for pure thallium, the middle curve for a solid solution containing 1.1% mercury, and the lowest curve for a solid solution containing 8.8% of mercury.

With this apparatus a number of cooling curves of pure thallium and of the various amalgams were made. They were usually started about  $15^{\circ}$  above the freezing points of the mixtures and continued to about  $40^{\circ}$  below. Three typical cooling curves are given in Fig. 1; one for pure thallium, one for an amalgam containing 98.9%; one for an amalgam containing 91.2% of thallium.

Discussing the pure thallium curve first, it is evident that at  $303.5^{\circ}$  the marked inflection occurs which indicates the freezing point (and melting point) of the pure metal. This temperature was found uniformly as  $303.5^{\circ}$  in all our pure samples. It is somewhat higher than the values

found by most of the other investigators, possibly because of greater purity of our specimens. At  $235.3^{\circ}$  comes another smaller inflection corresponding to the transition of  $\beta$  to  $\alpha$  thallium. This temperature also is higher than that of most other observations. Because of the small heat of transition, small quantities of impurity would tend to lower greatly the transition point, unless the impurity is isomorphous. This temperature is so near the standard temperature  $231.9^{\circ}$  (the melting point of tin) that it must have been accurately determined in our case.

Turning now to the cooling curves of the *amalgams*, we see, as would be expected, that the freezing point becomes less marked as the amount of mercury increases and that it is sometimes preceded by a slight depression

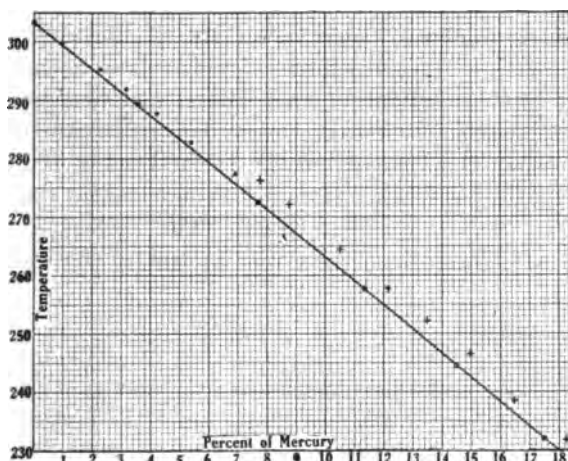


Fig. 2.—Liquidus curve (freezing points) of thallium amalgams.

The first breaks in three series of cooling curves (see Fig. 1) are here plotted to show the linear relation of temperature to mercury content. The last series (indicated by circles) was by far the most accurate.

due to supercooling. Instead of breaking sharply again at the downward turn, these curves show gradual decrease in freezing point as the freezing proceeds. This may be taken as definite evidence of the formation of a solid solution of mercury in thallium, agreeing essentially with the results of Pavlovitch and of Roos.<sup>21</sup> Of course the maximum temperature to which the mixture rose at the commencement of solidification after supercooling was taken as the freezing point, no measurable error resulting from the small amount of supercooling.

The results for the freezing point are sufficiently indicated by the accompanying graph, Fig. 2, in which they are carefully recorded, the graph

<sup>21</sup> Cf. Ref. 19.

taking the place of a printed table. In drawing the curve, the last most accurate and most comprehensive series (index 0) is given most weight. The other earlier series (from which small quantities of mercury had certainly evaporated during long heating) are indicated by other indices on the plot. These earlier values, lying closely together, serve to show that there is no minor inflection in the curve. The absence of inflection indicates that the solid phase produced at or in the neighborhood of the temperature of freezing with mixtures containing less than 20% of mercury consists of one or more solid solutions rather than a simple chemical compound.

At first sight, it might seem that the molecular freezing-point depression (*i. e.*, the depression produced by 1 gram-atom of mercury in 100 gram-atoms of solvent thallium) could be simply calculated from this curve, the result being  $3.95^{\circ}$ . Heycock and Neville,<sup>22</sup> from a study of the freezing points of dilute solutions of gold, silver, and platinum in thallium, concluded the molecular freezing-point depression for thallium to be  $6.31^{\circ}$ , from which they calculated the latent heat of fusion of thallium to be 5.12 calories per gram. Robertson<sup>23</sup> determined the heat of fusion of thallium as 7.2 calories per gram. The molecular freezing-point depression may be calculated from this datum by the well-known van't Hoff equation,

$$K = \frac{0.02 T^2}{L}$$

in which  $K$  is the molecular freezing-point depression,  $T$  the freezing point of the solvent on the absolute scale, and  $L$  the molecular latent heat of fusion of the solvent. In this case,  $T = 273^{\circ} + 303.5^{\circ} = 576.5^{\circ}$ ; and  $L = 7.2 \text{ calories} \times 204.1$ , therefore  $K = 4.53^{\circ}$ .

This result is much lower than the value,  $6.31^{\circ}$ , obtained by Heycock and Neville, but considerably higher than the value,  $3.95^{\circ}$ , obtained by direct experiment in the present investigation. The value  $3.95^{\circ}$  is doubtless too low because of the formation of a solid solution of mercury in thallium, as the formation of a solid solution may greatly change the freezing-point depression, tending to decrease it (even making it negative in the case of the solutions of lead in thallium).

If  $3.95^{\circ}$  is assumed to be correct, it leads to the value 8.3 for the latent heat of fusion of 1 g. of thallium.

Our solidus curve (melting point) agreed essentially with those obtained by Pavlovitch and by Roos by thermal methods.

### Densities of Concentrated Thallium Amalgams

The densities of the solid thallium amalgams were determined by a method similar to that used in the Harvard laboratories in the determina-

<sup>22</sup> Heycock and Neville, *J. Chem. Soc.*, 65, 31 (1894).

<sup>23</sup> Robertson, *ibid.*, 81, 1233 (1902).

tion of the density of lead from radio-active minerals.<sup>24</sup> Great care was used in the determinations, which were conducted at  $20.000^{\circ} \pm 0.003^{\circ}$ . Very pure dry toluene was used as the liquid to be displaced and the volume of the pycnometer was determined by pure water. Successive readjustments and weighings of the same sample never differed by more than 0.3 mg. The metal was cut into small pieces which could be slipped into the pycnometer, and all oxide was scraped from its surface. The metal was covered as soon as possible, and air bubbles removed either in a vacuum or by shaking (which gave identical results). Amalgams rich in mercury, which crumbled into fine crystals, gave trouble from oxidation, due possibly to the large surface exposed; this error was avoided by rapid manipulation and by avoiding as much as possible the disintegration of the amalgam. A preliminary series made with old amalgams of somewhat doubtful composition and giving irregular results was rejected. The second series given below was made with fresh amalgams made for this purpose. The samples were prepared from the same specimen of pure thallium by the successive addition of mercury, melting the metals together and cooling slowly. A small amount of mercury was lost during the successive fusions, but the amount was too small to cause any error beyond the limits of experimental error. The densities and specific volumes of the several amalgams reduced to the vacuum standard are given in the following table, in which each figure represents the mean of at least two determinations. The last value (for 80.35% thallium) came from crystals formed slowly from a more liquid amalgam, and separated centrifugally as well as possible from the residual liquid. The separation was incomplete, as appeared under the microscope; but from the result (knowing that the liquid has a density of 12.647 and contains 43.3% of thallium<sup>25</sup>) it is easy to calculate that if the solid contains 85.4% (as indicated by the e.m.f. measurements) the percentage of liquid in the mix-

TABLE II  
DENSITIES AND SPECIFIC VOLUMES OF THALLIUM AMALGAMS

Wt.-% of Tl in amalgam	Density of amalgam Mean value	Specific volume of amalgams		Diff. $\times 10^4$
		Obs.	Calc.	
100	11.849	0.08440	0.08440	0
99	11.873	0.08422	0.08429	- 7
97	11.874	0.08422	0.08408	+14
95	11.861	0.08431	0.08386	+45
93	11.896	0.08406	0.08365	+41
91	11.920	0.08389	0.08344	+45
89	11.918 (?)	0.08391 (?)	0.08323	+68
85.4	12.021 (?)	(0.08341) (?)	0.08285	+56
80.35	12.082			

<sup>24</sup> Richards and Wadsworth, 3rd, *THIS JOURNAL*, **38**, 221 (1916).

<sup>25</sup> Richards and Daniels, Ref. 4.

ture was 12% and the density of the solid crystals 12.021. Since, as will be shown, the percentage 14.6 of mercury is probably less than the truth, this value is probably also somewhat too small. The fourth column gives values calculated on the assumption that no volume change occurred on amalgamation, and the last column indicates the extent of the expansion on amalgamation.

These results cannot be considered as very satisfactory; probably protracted investigation would be necessary to obtain exact values. Especially with amalgams poor in thallium the structure of the solid must vary with the speed of cooling; moreover, under the best conditions the first crystals which appear must come from an environment richer in thallium than the later ones. Hence the samples cannot be uniform in composition, and may well change in volume on aging. In spite of these disadvantages, however, two facts appear clearly from the figures; first, that a sharp break in the curve appears at the 95% point, (the density having been but slightly altered by the mercury until after 5% had been added), and secondly that marked expansion occurs as a rule on amalgamation. This latter fact was known before as regards liquid amalgams. We have extended it to the solid state. The results will be plotted later in comparison with the other properties.

### Hardness of Amalgams

Hardness is a characteristic physical property, but one which, dependent upon several quite distinct magnitudes, is not easily defined.<sup>26</sup> None of the methods for determining hardness has proved wholly satisfactory, because of the varying influence of the tendencies determining this property. The methods are as follows: (1) resistance to scratching or cutting; (2) resistance to indentation when stressed either gradually or suddenly; (3) elastic reaction; (4) plastic flow<sup>27</sup> (as regards soft materials).

With thallium amalgams the first method shows qualitatively a distinct increase in hardness with the addition of small quantities of mercury. This method, however, especially with soft materials, does not give satisfactory quantitative results. We have, therefore, depended primarily on the second method.

Our first tests were made by noting the diameter of the depression produced by the sudden impact of a small hammer with a hemispherical face. Originally it had been intended to measure the height of the rebound of this hammer, which was raised by the suction of a rubber bulb to the top of the glass tube where it was conveniently held, to be released,

<sup>26</sup> C. H. Desch, "Metallography," 1918, p. 243.

Walter Rosenhain, "Introduction to the Study of Physical Metallurgy," 1914, p. 218.

C. V. Boys, *Proc. Phys. Soc. (London)*, 30, 83 (1918).

<sup>27</sup> Kurnakov and Zemczuzny, *Jahrb. Radioakt.*, 11, 1 (1914).

when desired, by pressure upon the bulb. The rebound, however, was too small for accurate measurement. Accordingly the use of this instrument<sup>28</sup> was abandoned as regards its original intention and the diameters of the indentations were measured, thus using the apparatus in the sense of the second method of determining hardness. The hammer was very small and the depression in thallium only 1.0 mm. in diameter.

These preliminary results could not be translated into the usual hardness numbers, but since the energy of the falling hammer was always the same, they serve as a good index of relative hardness.

Three series of samples of thallium were used in this test; first the samples which had been for 4 months under saturated thalious sulfate solution in the electrolytic cells; second, another set of similar samples which had been in the first place more slowly cooled during their original preparation; and third, 2 samples which had been carefully annealed for 18 hours at about 140°. Many measurements were made using both sides of the flattened samples. The annealing of the 97% and 93% samples was found to make no difference. Some of the samples, measured again after from 4 to 7 months, showed no significant change. A summary of average results is given in the following table.

TABLE III  
PRELIMINARY DETERMINATIONS OF HARDNESS  
(Shore scleroscope)

Wt.-% Tl	Average diameter of depression (in mm.)	
	First series	Second and third series
100	1.00	0.99
99	0.92	0.97
97	0.84	0.91
95	....	0.88
94	0.73	....
93	....	0.84
91	....	0.85
90	0.76	....
89	....	0.85
88	0.76	....

Evidently there is a marked increase in hardness up to about 6% of mercury, after which the hardness slowly diminishes in both series. The first series showed a greater increase with added mercury than the second. These results were qualitatively similar to those obtained by Pavlovitch,<sup>19</sup> but he found the maximum of hardness with 3% of mercury instead of with 6%.

The results, especially in view of the electromotive force and density measurements, were sufficiently interesting to warrant a more careful study. Accordingly, a more searching test of hardness was made by the

<sup>28</sup> The Shore scleroscope, dependent on elastic reaction.

Brinell method.<sup>29</sup> This is the most highly developed and generally used method and consists in pressing a hardened steel ball under a measured load into the surface of the material to be tested and measuring the diameter of the circular indentation produced.

We are indebted to Professor Albert Sauveur for his kindness in lending us his Brinell apparatus and in acquainting us with some of its subtleties.

If  $H$  = hardness number,  $L$  = load in kilograms,  $A$  = area in sq. mm. of the concave surface of the indentation, and  $R$  = the radius of the ball in centimeters, then  $H = L \sqrt[5]{R/A}$ , approximately.

We used a ball 1 cm. in diameter; hence the formula becomes  $H = L/A$ .

When a constant load is used the small actual deviation<sup>30</sup> of  $H$  from a truly linear relation to  $L$  becomes unimportant. An upward flow of material around the compression ball, forming a ridge on the rim of the indentation, sometimes complicates the matter. In our experiments this was unimportant except in the case of pure thallium, where the flow was downward instead of upward. Another but less serious complication (the deformation of the steel ball under the load) was not sufficient to affect our results seriously, and since we always used loads of either 50 kg. or 100 kg. in each of these series, the relative values in either series were entirely uninfluenced by it.

Time enters to some extent into the question since the indentation does not immediately attain its full magnitude. Experiments showed, however, that, with our specimens, the depressions produced in 10 seconds and in 30 seconds were essentially identical; therefore the latter period, always used in our work, was doubtless sufficient.

For the Brinell test large samples of the amalgams prepared for density determinations were employed. The cylinders of metal were about 2.20 cm. in diameter and from 0.8 to 1.8 cm. in thickness. They were provided with smooth parallel faces. The variation in thickness of the cylinders had no effect upon the results. Each sample to be tested was placed on a movable steel plate resting upon a heavy steel column and was carefully levelled. Contact between the surfaces of the specimen and the ball having been adjusted, the pressure was applied (by a hydraulic testing machine) attaining in 7 seconds its maximum, which was maintained for exactly 30 seconds. The diameter of the indentation was measured with a micrometer microscope. The higher pressure could not be used with the softer samples, since 100 kg. pressed the ball so deeply into

<sup>29</sup> Brinell, Communications, présentées devant le congrès international des méthodes d'essais de matériaux de construction. Paris, 3, 83 (1900). *Baumaterialienkunde*, 1900, p. 276.

<sup>30</sup> C. Benedicks, "Recherches Physiques et Physico-Chimiques sur l'acier au Carbone," Upsala, 1914, p. 75.

R. P. Devries, "Comparison of Five Methods Used to Measure Hardness," *Bur. Standards Tech. Paper*, 11, (1912).

the mass of thallium that a collar holding the ball was forced into the metal. The results were calculated with the help of a table giving  $L/A$  for different loads and diameters.<sup>31</sup> The diameters of depressions produced in thallium (with 50 kg. load) varied only between 6.0 and 6.1. The hardest amalgam (95% thallium) under the same pressure gave diameters of depression varying from 3.48 to 3.55 mm. Under 100 kg. load the diameters with this sample varied from 4.75 to 4.91. Below are given the averages of many determinations obtained in this way. The disintegrated crystalline macrostructure interfered with accuracy in the case of the 89% amalgam and entirely prevented the determination of hardness when more mercury was present.

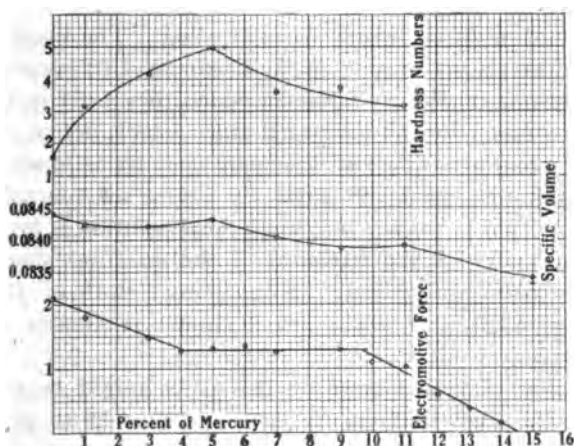


Fig. 3.—Hardness, specific volume, and e.m.f. of thallium amalgams.

The respective properties are plotted quantitatively as ordinates; the mercury contents of the several amalgams are plotted as abscissas. For hardness the usual Brinell numbers are used; the specific volumes are in cc. per gram; the unit of electromotive force is the millivolt.

TABLE IV  
HARDNESS OF SOLID THALLIUM AMALGAMS

Wt. % of Tl	Brinell hardness number	
	50 kg. load	100 kg. load
100	1.57	....
99	3.19	....
97	4.15	4.85
95	4.99	5.12
93	3.60	3.85
91	3.66	3.93
89	3.18	3.36

<sup>31</sup> Sauveur and Boylston, "Laboratory Experiments in Metallurgy," Cambridge, Mass., 1908, p. 54.



The hardness numbers show a marked maximum at 95% thallium under both 50 and 100 kg. load. The numbers with the different loads do not exactly agree. In general it has been observed in the past that with the Brinell test a heavier load is apt to give higher values for the hardness numbers. Possibly, moreover, the scale readings for the pressure were not exact, as the gage was not calibrated and the movement of the needle was small, since the gage was intended primarily for higher pressures. Nevertheless, the results are amply sufficient for our purpose. We were not concerned primarily with the absolute value of the Brinell numbers. Evidently the verdict of this method of testing hardness is essentially identical with that given by the improvised method with the Shore scleroscope.

The interpretation of the results is interesting. The hardness of a binary mixture depends not only upon the hardness of its constituents individually, but also upon the condition in which they exist in the mixture. Desch and Tammann have formulated rules which define some causes of the changing hardness of alloys.<sup>22</sup> Since mercury is much softer than thallium the mixtures should be softer than pure solid metal, supposing that no solution were formed. If a single solid solution is formed and no other complication exists the hardness of the mixtures should increase to a maximum with equimolecular proportions. Both of these suppositions are ruled out by our results, which show a maximum with 5% or 6% of mercury.

The appearance of a maximum at this place might be explained by assuming that the solid thallium molecule contains 15 to 20 atoms, but this explanation would demand that the second branch of the curve with increasing mercury should fall off much more rapidly in hardness than it actually does. A much more likely explanation, as will be seen, is that at 5% of mercury a new solid phase containing thallium in a different modification comes into existence. This is especially clear when the hardness numbers are compared with the results for electromotive force, density and melting point.

### Correlation of Results

Let us review the conclusions reached, in order to correlate them. The diagram (Fig. 1) will assist in the correlation. In Fig. 1 the more trustworthy values (except the linear freezing-point curve given in Fig. 2) are plotted in the same diagram. The horizontal axis represents the composition of the amalgams, and along the vertical axis are plotted first, the electromotive forces in millivolts, below, then the specific

<sup>22</sup> Desch, Ref. 26, p. 249.

Tammann, "Lehrbuch der Metallographie," 1914, p. 332. Cf. also Desch, *Trans. Faraday Soc.*, 10, 251 and 254 (1915).

Kurnakov and Zemczuzny, *Z. anorg. Chem.*, 60, 1 (1908).

volumes in cubic centimeters, and finally, above, the Brinell hardness numbers. All the properties unite in pointing to the existence of a solid solution of mercury in thallium up to 14.5%, which quantity appears to cause saturation. The linearity of the freezing-point (liquidus) curve had shown, as already stated, the absence of a definite compound at the melting temperature within this range. On the other hand, the three other curves in the diagram show striking inflections in the neighborhood of 5% of mercury, and two of them show inflections again with about 10% of mercury. What is the explanation of these inflections?

The electromotive force, representing free energy, is the most convenient starting place for the reasoning. Its curve (the lowest in the diagram) gives clear evidence of the existence at first of a single solid phase, which increased in mercury content until it contained about 4% of mercury. At this point, a second solid phase must have appeared, since the e.m.f. became constant.<sup>33</sup> This new solid phase existed in equilibrium with the first phase throughout the length of the horizontal portion of the curve down to 91% of thallium. At 96% the mixture must have consisted entirely of the first phase, while at 91% it must have consisted entirely of the second. As the thallium content decreased beyond this point, the second phase became manifest as a new crystalline form, and its composition changed until at 85.4% its potential became that of the 55% amalgam, showing that a liquid phase appeared at this point. Beyond this point the solid phase and the liquid phase must of course be in equilibrium until the solid disappears with less than 43.3% of thallium.<sup>34</sup>

The other properties confirm these conclusions. The data concerning hardness found in the present investigation likewise point to the solid solution of mercury in  $\alpha$ -thallium alone at 20° until about 5% of mercury has been added, and they are consistent with the assumption of the appearance of a second solid phase in the neighborhood of this point because here the hardness ceases to increase with added mercury.

The specific-volume curve reveals an increase of volume accompanying the mixing of mercury and thallium, which, as before, is an indication of the formation of a solid solution. The break in the continuity of the curve at 5% of mercury can only indicate a change in the number of phases at this point; and perhaps another change occurs also at about 11%. Thus it is essentially consistent with the two preceding curves. As al-

<sup>33</sup> The phase rule demands constancy of activity at constant pressure and temperature with 2 phases and 2 components.

<sup>34</sup> Richards and Daniels, Ref. 4. The appearance of the liquid phase between 86% and 85% was indicated also by the results of examination of the amalgam with a microscope, as an 85% amalgam was found to contain a small, but appreciable, quantity of liquid. A trace of liquid was found in freshly prepared 86% and 87% amalgams, but electromotive-force measurements showed that equilibrium had not here been established when the sample was examined.

ready stated, however, the experimental data concerning this property were not very satisfactory—more would be needed to make entirely sure of the slight breaks in the curve.

What now can be the second solid phase which exists in equilibrium with the first between the concentrations of about 4% or 5% and about 10% of mercury, and which afterward takes in more and more mercury until it finally dissolves?

A solid solution of mercury in  $\beta$ -thallium is the only substance which seems to be capable of producing effects consistent with the facts. The possible existence of this phase even at room temperatures under these conditions is easily shown.—The transition temperature of the  $\alpha$  to the  $\beta$  enantiotropic form is, as has been said, greatly affected by impurities.

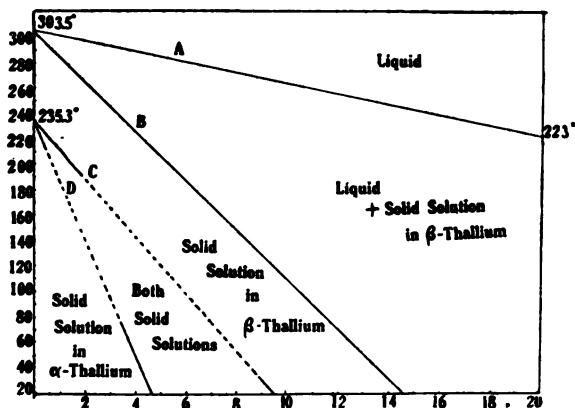


Fig. 4.—Phase diagram, showing freezing and melting temperatures, and analogously related transition limiting temperatures, in relation to mercury contents of concentrated thallium amalgams.

Pavlovitch showed that 1 atomic per cent. of mercury lowered it from 234.0° to 212°, at the same time decreasing markedly the intensity of the arrests in the cooling curves. With more mercury these arrests entirely disappeared, because of the gradual transition of the solid solutions. When in Fig. 4, the curve C, depicting change of transition temperature with concentration, is nevertheless extrapolated in a straight line (in analogy to the liquidus curve A in Fig. 4, which was shown to be very nearly linear), it appears that a 90.5% amalgam corresponds to transition at 20°. Hence any amalgam stable at 20°, poorer in thallium than about this amount, must contain only the  $\beta$  form of this metal. This is probably the new solid solution which appeared as the well-marked crystals of near-cubic form already mentioned. Evidently the solid amalgam in equilibrium with any liquid amalgam must be this  $\beta$  solid solution.

Along and immediately to the left of this curve C, the solid solution of mercury in  $\beta$ -thallium must be mixed and in equilibrium with the solid solution of  $\alpha$ -thallium,<sup>35</sup> which latter solution must, saturated as it is, be richer in thallium than the former. As the total percentage of mercury is diminished (between 10% and 5%) at any one temperature, the proportion of  $\alpha$ -thallium must increase, until the mercury present corresponds to the exact saturation point at 20° of the  $\alpha$ -amalgam (about 5% of mercury). At this point, with further decrease in mercury, the  $\beta$  phase will entirely disappear. The curve D represents this latter dividing line.

Thus, five fields are established in the thermal equilibrium diagram, each of which is duly labeled on the accompanying graph. This explanation seems to elucidate adequately all the widely diverse phenomena. Evidently the metals expand on adding mercury to form the  $\alpha$  solid solution, but no great change of volume of the constituents occurs when additional mercury gradually changes the  $\alpha$  into the  $\beta$  modification. Hence occurs the break in the specific volume curve at 95% thallium. Evidently, too, both solid solutions are harder than pure thallium, the  $\alpha$  solid solution being somewhat the harder of the two. That the new phase is a solid solution in  $\beta$ -thallium rather than a compound (such as  $Tl_7Hg$  or  $Tl_4Hg$ ) is probable, not only because a compound of this kind is *per se* unlikely, but also because it should have a lower potential than a solid solution in  $\alpha$ -thallium containing the same amount of mercury, whereas in fact the new phase, although containing much more mercury than the original  $\alpha$  phase, nevertheless is in equilibrium with it.

If the line in Fig. 3 which represents the potentials of amalgams constituting the second phase (containing presumably  $\beta$ -thallium) is produced to meet the electromotive-force axis at a composition of 100% thallium, it should give approximately the potential of pure supercooled  $\beta$ -thallium against a 55% thallium amalgam at 20°. The result obtained by this extrapolation is 3.8 millivolts, while the potential of pure compact  $\alpha$ -thallium against a similar amalgam has been found to be 2.1 millivolts. The difference between these values (1.7 millivolts) should be approximately the difference of potential between the two modifications of thallium at 20°. On account of the uncertainty of the extrapolation, the result cannot be regarded as accurate; but it should, at least, indicate the order of magnitude of the quantity. From this it may be calculated that at 20° the free energy content of supercooled  $\beta$ -thallium would be nearly 40 calories per gram atom higher than that of the compact  $\alpha$ -modification. This difference is nearly three times that found for spongy thallium, which could not, therefore, have been metastable  $\beta$ -thallium.

As already hinted, the nature of the case clearly prohibits great exact-

<sup>35</sup> Roozeboom has shown such a field as that included between the lines C and D in our diagram to be theoretically necessary. *Z. physik. Chem.*, 30, 417 (1899).

ness in the data for these solid amalgams. None of them could have been perfectly homogeneous, since the portion which first separated on cooling must have been richer in thallium than that which followed. The electromotive force would indicate the surface conditions, which might not represent the true average. The hardness, and especially the density, probably represent a fairer average of the whole mass, but even these latter phenomena may be much influenced by speed of cooling, which might affect not only the magnitude but also the position of the maxima of the curves. Possibly to such causes may be ascribed the difference in detail between our results for hardness and those of Pavlovitch, which nevertheless qualitatively agree with ours. More satisfactory results might be obtained by quenching the amalgams suddenly in very cold oil. For this extension of the work, time has not yet been found. We hope to continue the study later.

Similar considerations lead to the belief that the percentage of mercury, 14.5%, indicated for the saturation point of solid  $\beta$ -thallium at 20° may be less than the true value. Probably crystals separated from a large mass of saturated liquid amalgam immediately in the neighborhood of 20° would contain somewhat more than 15% of mercury, even if all the superficially adhering liquid could be removed.

In spite of these inherent experimental difficulties of the problem, which would not be easy wholly to eliminate, it seems probable that the picture here presented of the equilibria between mercury and large concentrations of thallium represents the essential characteristics of these equilibria, and that later investigations are likely to affect the outcome only in minor details.

We are indebted to generously granted funds from the Carnegie Institution of Washington as well as from an anonymous benefactor of the University for most of the apparatus and thallium employed.

### Summary

1. Pure thallium in compact form is definitely shown to possess at 20° an electrode potential 2.1 millivolts higher than saturated thallium amalgam. When immersed in a solution normal in thallos ions and connected with a normal calomel electrode, the total potential 0.6192 volt is indicated at 25°. The potential of pure thallium is not influenced by quenching the metal, which is so soft that no important strain can exist in it.  $\alpha$ -Thallium is the only phase of the pure metal stable at room temperatures.

2. Finely divided electrolytic thallium sponge gives a potential 0.6 millivolts higher than the compact fused form. The difference is probably due to the fine state of division, and disappears on long standing. The

the removal of extraneous and included water, with the retention of the combined water, appear to have received little attention. Most frequently the procedure has consisted in drying the moist crystals between filter papers<sup>4</sup> or in exposure to the air for a limited time.<sup>5</sup> We have found that samples thus prepared come quite surprisingly close to the theoretical composition, usually showing an excess of water as low as 0.3 to 0.5%; by a happy compensation of errors they might contain still less, but as the conditions are not reproducible, the method cannot be depended upon if a high degree of accuracy is desired.

The property of retaining included water in considerable amount is not peculiar to oxalic acid but it is well known that the phenomenon is general. Richards, in his thorough study of this property, says,<sup>6</sup> "It is no careless exaggeration to state that in all my chemical experience I have never yet obtained crystals from any kind of solution entirely free from accidentally included mother-liquor; and I have, moreover, never found reason to believe that anyone else has. The amount of the inclosure varies from perhaps 0.01 to 0.5% of the total weight of the crystals." It is apparent therefore that the presence of included water is to be expected in any hydrated compound which may be proposed as a standard, and since from the nature of a hydrate high temperatures cannot be used to facilitate its removal, we have a source of error not easily avoided. The method which we have adopted as minimizing this error consists simply in powdering the crystals in a porcelain mortar until they pass a 100-mesh sieve. This operation apparently breaks down very largely the cells which contain the water, and the large increase in surface permits a more speedy removal of water from the remaining unbroken cells. The crystals of oxalic acid are brittle and easily powdered; we have not been able to observe that there is any loss of water of hydration due to the heat of crushing. By this procedure the amount of included water may be quickly reduced to a very few hundredths of a per cent. as will be shown in the experimental part following.

In order to accomplish the evaporation of the superficial and included water without loss of water of combination, it is of course necessary to keep the crystals in an atmosphere in which the aqueous tension is less than that of the saturated solution and equal to or greater than the vapor tension of the hydrate. Recent measurements by Baxter and Lansing<sup>7</sup> have shown that this vapor tension is low, rising from 1.15 mm. at 15° to 2.65 mm. at 25°, the usual range of laboratory temperatures. We have been able to find record of only one recommendation of a

<sup>4</sup> Thiele and Dechert, Mohr, Maumené, Ref. 3.

<sup>5</sup> Fresenius, Ref. 2.

<sup>6</sup> Richards, *Proc. Am. Phil. Soc.*, 42, 28 (1903).

<sup>7</sup> Baxter and Lansing, *THIS JOURNAL*, 42, 419 (1920).

desiccating agent suited for this compound: Richards,<sup>8</sup> in his article on the rate of dehydration of crystallized salts, states "crystallized oxalic acid, so much used in making standard solutions, is best prepared by placing the powder over sulfuric acid of specific gravities 1.20 to 1.50; for the crystallized substance does not lose an essential amount of water at 22° in an atmosphere containing aqueous vapor at a tension of 4 mm.; while the aqueous vapor tension of its saturated solution is more than 15 mm." The vapor tension of sulfuric acid of the densities recommended by Richards is about 4 mm. to about 15 mm. There is no doubt that this desiccating agent is suited to the purpose. It is, however, open to the objection that its vapor tension varies with the water content of the acid, so that in time the acid chosen, having become diluted with water taken up from the air, will show too great a vapor tension to accomplish its purpose. Speaking more generally, it may be stated that any desiccating agent chosen, with the exception hereafter noted, will, if in equilibrium with the oxalic acid at one temperature, be out of equilibrium at some other temperature such as may be met with in laboratory practice, since the vapor tension curves of the desiccating agent and the oxalic acid will not vary uniformly with change of temperature.

We have, accordingly, made use in our experiments of the principle that a hydrate, its next lower hydrate and water vapor form a univariant system, in which a saturated solution (represented here by the surface water or included water) must at any temperature dry up to form the hydrate only. The desiccating agent selected, a mixture of hydrated oxalic acid and anhydrous acid, is easily prepared by heating the hydrate in a large porcelain dish upon a water-bath for a few hours, which produces sufficient conversion into anhydrous compound to serve acceptably. An ordinary desiccator, fitted with a layer of this preparation an inch in depth is sufficient to dry a considerable quantity of hydrate for use as a standard. The various forms of apparatus devised for hastening the drying of the hydrate will be described below.

In principle, the method which we have found best suited to give a hydrate of constant composition consists in recrystallizing the oxalic acid from water until free from non-volatile impurities, draining, freeing from most of the superficial water by standing over partially dehydrated oxalic acid, grinding to pass a 100-mesh sieve, and finally drying to constant weight again over the same desiccating agent. We have tested the crystals thus prepared for their oxidimetric value by titration with potassium permanganate solution.

### Experimental Part

The weights used in the experimental work were calibrated according to the method of Richards; the balance used for weighing the oxalic acid or the sodium oxalate had

<sup>8</sup> Richards, *Proc. Am. Acad. Arts Sci.*, 33, 26 (1897).

a sensitivity sufficient to give an accuracy of 0.1 mg., and that used for weighing solutions in the weight burets gave an accuracy of 1 mg.

Sodium oxalate was used as the ultimate standard of the work, the salt being Sample No. 40 from the Bureau of Standards; large quantities of the standard were first heated to 105° in an electric oven for 5 hours and kept in a desiccator over phosphorus pentoxide, from which small quantities were taken for further heating during 30 minutes immediately before use. Two permanganate solutions were prepared, one directly from a commercial analyzed "Reagent," and the second after two recrystallizations of the same material from twice distilled water. In each case the solution was filtered through washed asbestos immediately after preparation and again after an interval of some days through a Monroe platinum crucible. The water used was in all cases twice distilled, and the bottles, which were of 6 to 10 liters capacity, were of good quality glass; the solutions were protected from the action of light when not in use. The two solutions did not differ widely in their stability, as shown in the analyses of Table I.

TABLE I  
STANDARDIZATION OF POTASSIUM PERMANGANATE SOLUTIONS  
Solution No. 1

Elapsed time Days	$\text{Na}_2\text{C}_2\text{O}_4$ G.	$\text{KMnO}_4$ soln. G.	$\text{KMnO}_4$ soln. equiv. to 1 g. of $\text{Na}_2\text{C}_2\text{O}_4$ G.	Av. G.
0	0.2400	54.240	226.00	225.98
	0.2401	54.262	226.00	
	0.2399	54.205	225.95	
24	0.2417	54.618	225.97	226.01
	0.2399	54.219	226.01	
	0.2417	54.634	226.04	
52	0.2405	54.361	226.03	226.05
	0.2399	54.231	226.06	
	0.2404	54.343	226.05	
Solution No. 2 (recrystallized $\text{KMnO}_4$ )				
0	0.2400	53.914	224.64	224.58
	0.2406	54.031	224.57	
	0.2412	54.155	224.53	
33	0.2412	54.185	224.64	224.65
	0.2402	53.958	224.63	
	0.2312	51.948	224.68	
67	0.2402	53.957	224.63	224.65
	0.2403	53.989	224.67	
	0.2404	54.003	224.64	

In the titrations of sodium oxalate or of oxalic acid against the permanganate, the procedure followed was that recommended by McBride;<sup>9</sup> the solutions were kept at 70° during the titrations, the acid concentration maintained constant by use of 10 cc. of 1:1 sulfuric acid in 250 cc. of solution, and the permanganate solution added slowly throughout. In order to minimize experimental errors, weight burets were used throughout, the greater part of the titration being performed with a fifteenth weight-normal permanganate solution, while the end-point was obtained by use of a second weight buret containing permanganate of just  $1/10$  the concentration of the first. All

<sup>9</sup> McBride, *THIS JOURNAL*, 34, 393 (1912).



titrations were carried out by daylight, and the end-points matched with a permanent color standard made by addition of a very little cobalt nitrate to 250 cc. of water in a flask similar to those used in the titrations, the color value of which in terms of permanganate solution was determined by a series of comparisons; this value was regularly subtracted from the titration end-point. All analyses were performed in triplicate, and all analyses are included in the tables given.

In Table I are given the analyses of the two permanganate solutions which were used in the investigation, three dates being selected to cover the period of the work. The figures of Col. 1 give the elapsed time in days between the standardizations.

From the foregoing table it appears that the maximum variation in any group of three analyses is 0.11 g., or 0.048%, and the average variation 0.058 g. or 0.025%; the maximum variation from the mean is 0.06 g. or 0.026%, and the average variation from the mean is 0.033 g.

TABLE II  
HISTORY OF OXALIC ACID CRYSTALS EXPOSED TO AIR

	Sample I (Dec.-Mar.) (Large crystals) 4.0981 g.	Sample II (Dec.-Mar.) (Small crystals) 3.9150 g.
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Elapsed time Days	Total loss in weight Mg.	Total loss in weight Mg.
1	....	....
2	5.0	40.6
3	5.3	41.8
4	5.8	42.1
5	5.9	42.2
7	6.0	42.2
8	6.2	42.3
9	6.4	42.5
11	6.4	42.7
12	6.5	42.8
19	6.7	43.1
28	7.3	43.4
56	7.9	43.7
112	10.8	47.4
122	11.2	48.0

## ANALYSIS

$\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ G.	$\text{KMnO}_4$ soln. G.	$\text{KMnO}_4$ soln. equiv. to 1 g. of acid G.
0.2296	54.744	238.43
0.2300	54.851	238.48
0.2297	54.793	238.54

Av. 238.48

Required by calc. 238.82

Error in composition 0.34  
or -0.142%

## ANALYSIS

$\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ G.	$\text{KMnO}_4$ soln. G.	$\text{KMnO}_4$ soln. equiv. to 1 g. of acid G.
0.2303	54.997	238.81
0.2302	54.952	238.71
0.2301	54.927	238.71

Av. 238.74

Required by calc. 238.82

Error in composition 0.08  
or -0.033%

Sample I (Aug.-Nov.) (Large crystals) 4.125 g.			Sample II (Aug.-Nov.) (Small crystals) 4.000 g.		
Elapsed time Days	Total loss in weight Mg.		Total loss in weight Mg.		
1	....		....		
2	9.6		30.4		
3	10.0		30.2		
5	10.0		31.4		
6	10.9		31.7		
8	11.1		31.9		
10	12.0		32.0		
12	12.1		32.4		
14	12.1		32.3		
21	13.2		33.7		
82	17.2		38.5		
ANALYSIS			ANALYSIS		
$\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ G.	$\text{KMnO}_4$ soln. G.	$\text{KMnO}_4$ soln. equiv. to 1 g. of acid G.	$\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ G.	$\text{KMnO}_4$ soln. G.	$\text{KMnO}_4$ soln. equiv. to 1 g. of acid G.
0.2299	54.772	238.40	0.2300	55.015	239.20
0.2303	54.898	238.37	0.2303	55.098	239.25
0.2298	54.805	238.48	0.2305	55.165	239.33
	Av.	238.42		Av.	239.26
Required by calc.		238.82	Required by calc.		238.82
Error in composition		0.40	Error in composition		0.44
or		-0.163%	or		+0.184%

or 0.015%. From this it may be deduced that a series of analyses may be depended upon to about 0.02%. This is also the limit of accuracy of the weighings, which may be in error by 0.05 mg. It also appears that the permanganate solutions lost in strength somewhat in a period of 2 months, the loss being 0.07 g. or 0.031% in each case; apparently the solution made from the recrystallized salt reached equilibrium in the first month. For the purposes of comparing the oxalic acid with the sodium oxalate, discussed later, the value of the permanganate at the nearest date was used.

The oxalic acid used in the experiments was a sample of Baker's analyzed c. p. preparation, which was recrystallized three times from hot water. The material thus obtained gave no test for sulfates or chlorides, and no weighable or detectible residue upon the sublimation of a 4g. sample from a platinum crucible. In order to test the behavior of crystals of the size usually obtained by recrystallization, the material was treated by two different procedures in the third recrystallization; one part of the solution was surrounded by ice water, and cooled as quickly as possible,

with stirring, so as to obtain fine crystals, while the other portion was surrounded by hot water and cooled as slowly as possible, the resulting crystals being quite large. It would seem that these two procedures should give the maximum and minimum size of crystals likely to be met with in ordinary laboratory practice.

In order to determine the rate at which these crystals lose their included water, they were exposed, after drainage, to the air of the laboratory for extended periods of time, during which they were protected from dust and kept away from laboratory fumes. The history of each sample was determined by careful weighings made at intervals beginning with the end of the first 24 hours and, finally, at the end of 3 to 4 months, by an analysis with the standard permanganate solution. The results are given in Table II.

The four samples tested, underwent a small but continuous loss of weight during periods of 3 to 4 months, when exposed to the atmospheric conditions of the winter months as well as those of late summer and early autumn. At the end of the periods of exposure, the crystals showed unmistakable evidence of efflorescence, and white stains on the watch-glasses indicated that there had also been periods of slight deliquescence. Constancy of composition cannot, it appears, be obtained by the method of direct exposure to the air. The crystals are, however, not as far from the desired composition as might be expected, the variation being at the end of the period between  $+0.184\%$  and  $-0.142\%$ , as determined by analysis; the number of grams of permanganate solution required (Solution No. 2, third standardization) has been calculated by taking 224.65 as the amount required per gram of sodium oxalate, and using 134.01 and 126.048 as the molecular weights of oxalic acid and sodium oxalate respectively. The analytical data for the samples exposed in the fall have been multiplied by a factor to bring the normality of the permanganate to that used in the earlier determinations, so that comparisons may be simpler.

It may be concluded from the preceding table that crystals as ordinarily prepared contain several tenths of a per cent.<sup>10</sup> of included water when superficially dry (as after the first 2 or 3 days of exposure), and that exposure to air permits a gradual loss of included water and water of hydration as well, so that the composition may pass through the theoretical value (by the compensating errors of partial efflorescence and small inclusion of water) to a value in which the water is less than that required by the formula.

Experiments were conducted to determine whether ordinarily prepared crystals, as described before, would come to the correct composition if

<sup>10</sup> Preliminary work done some time ago by Sister M. Augustina Brobston showed that the crystals contained from 0.30% to 0.43% of included water, as determined by their acidimetric value compared with analyzed  $H_2SO_4$ .

exposed to an atmosphere of the correct vapor pressure. The samples were set in ordinary desiccators over the mixture of anhydrous and hydrated oxalic acid, which will be referred to hereafter as the desiccating mixture; the results are given in Table III.

TABLE III

HISTORY OF OXALIC ACID CRYSTALS DRIED OVER DESICCATING MIXTURE

Elapsed time Days	Sample III (Large crystals) 3.9075 g.	Sample IV (Small crystals) 3.9753 g.
	Total loss in weight Mg.	Total loss in weight Mg.
1	....	....
2	40.2	100.2
3	41.2	100.8
4	41.4	100.8
5	41.8	101.0
6	42.1	101.2
7	42.3	101.3
8	42.4	101.4
9	42.5	101.6
10	42.5	101.7
17	44.6	102.5
24	45.3	103.5
31	46.3	104.9
38	47.3	105.6
47	48.2	106.6
74	49.6	108.2
126	54.6	113.8
137	54.8	114.3

## ANALYSIS

## ANALYSIS

$\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ G.	$\text{KMnO}_4$ soln. G.	$\text{KMnO}_4$ soln. equiv. to 1 g. of acid G.	$\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ G.	$\text{KMnO}_4$ soln. G.	$\text{KMnO}_4$ soln. equiv. to 1 g. of acid G.
0.2304	54.888	238.23	0.2301	54.856	238.40
0.2302	54.853	238.28	0.2300	54.836	238.41
0.2301	54.834	238.30	0.2299	54.821	238.46
	Av.	238.27		Av.	238.42
Required by calc.		238.82	Required by calc.		238.82
Error in composition		0.55	Error in composition		0.40
	or	-0.230%		or	-0.167%

The crystals thus treated showed no evidence of efflorescence at the end of the period of 4 months, but still contained relatively large amounts of included water (0.167 to 0.230%). It is clear, therefore, that the material cannot be brought to a fixed and correct composition by any sort of exposure, as long as the crystals are of considerable size, and that powdering of the material is a necessity if an accurate standard is desired.

In order to obtain a finely powdered sample for use as a standard, it was found necessary to secure a superficial dryness suitable for crushing by placing the ordinary crystals in a desiccator over the desiccating mixture; if they have been previously whirled in a centrifugal machine they become dry enough for further treatment in a day's time. They were then crushed in a glazed porcelain mortar, passed through a 100-mesh sieve of copper gauze, and tested in the several ways given below.

The simplest procedure, as regards effort, was found to consist in letting the powder attain equilibrium in the desiccator. Tests as to the effectiveness of this method are given in Table IV, in which the changes of weight have been followed over a time interval of 3 months and checked by an analysis at the end of the period. Permanganate solution No. 2, third standardization, was again used.

TABLE IV  
HISTORY OF PULVERIZED OXALIC ACID CRYSTALS IN DESICCATOR OVER DESICCATING MIXTURE

Sample I (Large crystals, ground) 3.6992 g.			Sample II (Small crystals, ground) 3.6029 g.		
Elapsed time Days	Total loss in weight Mg.		Total loss in weight Mg.		
1	...		...		
2	0.0		0.0		
3	0.1		0.1		
4	0.2		0.1		
13	0.3		0.3		
21	0.4		0.4		
42	0.4		0.5		
97	1.1		1.0		
Analysis			Analysis		
H <sub>2</sub> C <sub>2</sub> O <sub>4</sub> ·2H <sub>2</sub> O G.	KMnO <sub>4</sub> soln. G.	KMnO <sub>4</sub> soln. equiv. to 1 g. of acid G.	H <sub>2</sub> C <sub>2</sub> O <sub>4</sub> ·2H <sub>2</sub> O G.	KMnO <sub>4</sub> soln. G.	KMnO <sub>4</sub> soln. equiv. to 1 g. of acid G.
0.2301	54.959	238.85	0.2300	54.940	238.87
0.2299	54.919	238.88	0.2304	55.032	238.85
0.2298	54.886	238.84	0.2302	54.995	238.90
Av.		238.86	Av.		238.87
Required by calc.		238.82	Required by calc.		238.82
Error in composition		0.04	Error in composition		0.05
or		+0.017%	or		+0.021%

The crystals thus prepared vary from the theoretical composition by only about 0.02%, in the direction of deficiency of water; the variation is of the same magnitude as the errors of analysis. If the loss during standing after the first day, which amounts to 1.0 mg. and 1.1 mg., respectively, be added, it appears that at the end of that period also the

composition agrees with theory within 0.02%, in the direction, however, of excess of water.

Attention was given to the problem of hastening the drying of the powder, so that the time required for the preliminary and final drying might be reduced to a matter of hours in place of the 2 days necessary when a desiccator is used. It seemed probable that that end could be secured if a current of air of correct aqueous tension could be substituted for the closed space of the desiccator. A preliminary apparatus devised for this purpose consisted of a small bell jar, in which the crystals were placed in a crystallizing dish, and the apparatus inserted into a larger jar of mercury; the neck of the bell-jar was fitted with an outlet-tube and an inlet-tube, the latter being connected with two 15cm. U-tubes filled with the usual desiccating agent, and the former running to a guard tube and thence to a water pump. When a moderately rapid stream of air was drawn through the apparatus, it was found that the preliminary drying could be accomplished in 30 to 60 minutes, and the final drying of the powder in 1 hour. During the course of the experiment, however, it was found that the action of the current of air for a period of 17 to 20 hours resulted in a distinct loss of water, analysis showing a deficit of 0.16% and 0.22% of water in two groups of analyses. The explanation appears to be that the aqueous tension of the air used (it being mid-winter) was too low, and that equilibrium was not attained in the rapid passage of the air through the drying tubes. To eliminate this source of error, a wash-bottle containing a saturated solution of oxalic acid was set at the beginning of the train; the air passing through this should take up more than the necessary amount of water, which should be reduced to the correct amount in passing through the U-tubes. The use of this device ended the apparent dehydration of the crystals. In Table V are given the results obtained with the train, the first three analyses being conducted without

TABLE V  
POWDERED OXALIC ACID DRIED IN AIR CURRENT IN BELL-JAR

Time of drying Hours	$\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ G.	$\text{KMnO}_4$ soln. G.	$\text{KMnO}_4$ solution equiv. to 1 g. of acid G.
1	0.2300	55.272	240.31
2	0.2297	55.194	240.29
3	0.2304	55.254	240.25
20	0.2304	55.372	240.33
20	0.2292	55.089	240.35
20	0.2303	55.339	240.29
			Av.
Required by calc.			240.27
Error in composition			0.03
or			0.012%

the use of the saturated solution and the second three with its use. Potassium permanganate No. 1, second standardization (see Table I), was used in the analyses.

It appears from Table V that the powder is completely dried in as short a time as 1 hour, and that there is no detectible change in 20 hours in a current of air properly prepared. It remained only to modify the apparatus if possible in the direction of greater simplicity and convenience. The apparatus which we have found best suited is made from a 30cm. length of rather wide combustion tubing, into which the crystals are inserted in a porcelain combustion boat of the usual form; the U-tube of the desiccating agent and, for safety's sake, the wash-bottle of saturated oxalic acid solution are connected as before, and the preliminary and final drying carried on for 30 minutes and 1 hour respectively. Table VI gives a series of analyses conducted in this fashion, but without the use of the saturated solution in the train. Permanganate solution No. 1, second standardization, was used in the analysis.

TABLE VI  
POWDERED OXALIC ACID DRIED IN AIR CURRENT IN COMBUSTION TUBING

Time of final drying Hours	H <sub>2</sub> C <sub>2</sub> O <sub>4</sub> ·2H <sub>2</sub> O G.	KMnO <sub>4</sub> solution G.	KMnO <sub>4</sub> soln. equiv. to 1 g. of acid G.
1	0.2300	55.286	240.37
1	0.2309	55.517	240.44
1	0.2304	55.357	240.26
1	0.2310	55.516	240.33
2	0.2297	55.210	240.36
3	0.2301	55.295	240.31
1	0.2295	55.153	240.32
2	0.2310	55.511	240.31
3	0.2299	55.245	240.30

	Av.	240.33
Required by calc.		240.27

Error in composition	0.06
or	+0.025%

From the series of analyses obtained it may be stated that hydrated oxalic acid, as prepared above, agrees with sodium oxalate in reducing effect upon permanganate to within 0.025%, the acid appearing to have a reducing value greater by that amount than the value calculated from its molecular weight. This small difference is of the same order as the error in the analysis, but from the frequency of its occurrence it does not seem to be mere chance error. It may be explained possibly as due to that amount of error in the composition of the Bureau of Standards sodium oxalate, or, as seems more probable, to the occurrence of inequalities in temperature in the desiccator during laboratory working conditions,

which might produce a partial efflorescence of the exposed hydrate. The point is left unsettled at this time.

It is our purpose to compare oxalic acid prepared in this manner with other standards used in acidimetry, and to test the same method of preparation in the study of other hydrated compounds used as standards, including Mohr's salt and copper sulfate.<sup>11</sup>

### Summary

1. Crystals of hydrated oxalic acid as usually prepared from aqueous solution contain several tenths of a per cent. of included water, which is not wholly lost by 4 months' exposure to atmospheres of the same aqueous tension as the crystals or higher.

2. Crystals superficially dry will lose this included water in about 24 hours' time if ground to pass a 100-mesh sieve and set in an atmosphere of an aqueous tension in equilibrium with the hydrate.

3. A mixture of hydrated and anhydrous oxalic acid is the only desiccating agent giving an aqueous tension in equilibrium with the hydrate at all temperatures.

4. The powdered hydrate can be dried in about 1 hour's time in a current of air passed over this desiccating mixture, so that its oxidimetric value agrees with that of sodium oxalate within 0.025%.

NEW YORK, N. Y.

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[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, UNIVERSITY OF WASHINGTON]

## THE MEASUREMENT OF OVERVOLTAGE

BY HERMAN V. TARTAR AND HARMON E. KEYES

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### Introduction

It is now generally agreed that overvoltage is an electromotive force which acts counter to the applied e.m.f. during electrolysis. For the purpose of this paper hydrogen overvoltage is defined as an e.m.f. which is the difference of potential between a reversible hydrogen electrode and an electrode surface at which hydrogen gas is being formed from hydrogen ions by electrolysis, both potential measurements being referred to the same electrolyte.

Opinion has been divided as to the proper method of determining overvoltage, especially when high and varied current densities are used. Two distinct methods of measurement have been employed; (1) the commu-

<sup>11</sup> The possible use of a mixture of hydrate and anhydrous compound as a drying agent came to the attention of one of us in conversation some 20 years ago with Prof. Robert W. Hall, then professor of analytical chemistry at New York University. It is not remembered that Professor Hall claimed originality for the idea, and we have not been able either to find its origin or to hear that it has ever been tested.



tator method in which the current is periodically interrupted with a rapidly rotating commutator; (2) the direct method, in which the electrode potential is determined while the current is flowing. The latter method always gives the higher result. In either case the measurements are made with a hydrogen electrode or indirectly with any standard electrode. It is unnecessary here to give any review of the quite voluminous literature reporting the results obtained by these methods. The methods themselves will be presented more fully in a later part of this paper.

Any correct method of measurement must fulfil the first two and, if the current is interrupted, all of the following requirements: (1) neither the size nor shape of the containing vessel nor the distance between anode and cathode should exert any influence; (2) by definition, the value found must represent an e.m.f. and not a resistance; this entails the elimination of appreciable potential drops due to resistance of electrolyte or any resistance of whatever nature at the surface of the electrode; (3) if measurement be made while the current is interrupted the counter e.m.f. must be instantaneously constant and have the same value as when the exciting current is flowing; there must be no fall of potential during the period of interruption.

The aim of the work here presented was to compare simultaneously the two methods of measurement by obtaining, at a certain point in the procedure, a potential of known value. To secure this condition advantage was taken of the fact that a metal, such as zinc, which is above hydrogen in the electromotive series, may be deposited electrolytically from a strongly acid solution of its salts, upon a cathode of a metal of lower overvoltage, as for example copper or nickel, by simply raising the current density until a transition point is reached when zinc is deposited instead of hydrogen. The deposition of zinc occurs, of course, when the cathode surface has reached the potential of zinc in the electrolyte.

By way of acknowledgment, the writers wish to state that they were led to this method of attack through the work of U. C. Tainton<sup>1</sup> in which he sought to ascertain the critical current densities necessary for the deposition of zinc upon metals of lower overvoltage.

## Experimental Part

**Apparatus and Materials.**—The apparatus consisted of a Leeds and Northrup potentiometer of the smaller type, a Leeds and Northrup galvanometer of the portable lamp and scale type, a rotating commutator driven by an electric motor, lead storage cells, resistances, normal calomel electrode, hydrogen electrode and experimental cell. The arrangement of the apparatus is shown in Fig. 1.

The electrodes of the experimental cell were circular discs 1 cm. in diameter, soldered on one side to copper wires which were sealed into glass tubes. This side of the electrode

<sup>1</sup> Unpublished work now being presented to the American Electrochemical Society. Mr. Tainton was assisted by one of us, Keyes.

and any exposed copper wire were completely covered with sealing wax. Cathodes of copper, nickel, lead, iron and bright and platinized platinum were used with a lead anode. Previous to each test the electrodes were cleaned with nitric acid, if necessary, and then rubbed with No. 00 sandpaper to give a surface as nearly uniform as possible.

The commutator used was carefully tested for short circuits and mechanical deficiencies, to avoid any errors due to faulty construction or improper manipulation.

The electrolytes used were made of distilled water and "c. p. Analyzed" sulfuric acid and zinc sulfate. Further purification of these chemicals was found not to modify the experimental results.

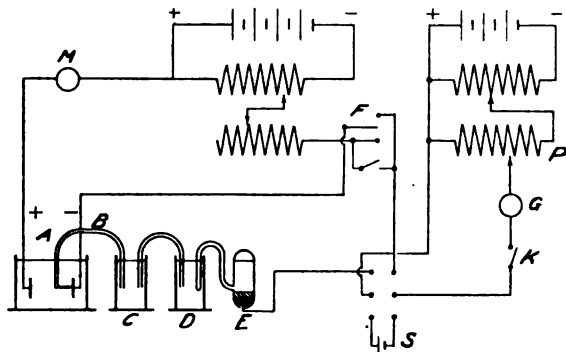


FIG. 1.

- |                         |                         |
|-------------------------|-------------------------|
| A, Exp. cell            | G, Galvanometer         |
| B, Capillary connection | K, Key                  |
| C, Cell electrolyte     | P, Potentiometer        |
| D, Sat. KCl solution    | S, Standard Weston cell |
| E, N-Calomel electrode  | M, Milli-ammeter        |
| F, Commutator           |                         |

Results of duplicate tests confirmed the observations of previous workers that overvoltage varies with the nature of the electrode surface, and also with time. For this reason it was difficult, after cleaning an electrode, to obtain results closely agreeing with former values obtained with the same electrode under similar conditions of time and current density. Since the main purpose of these experiments was to determine overvoltage by the two methods of measurement, at a given time, and to compare the two values with a known potential, any change of overvoltage by altering the degree of smoothness of the electrode surface was considered immaterial.

Throughout the paper reference is made to the value of the zinc potential. This was obtained in the following manner.

A lead electrode and a zinc electrode, upon which a new surface of zinc had been deposited electrolytically, were placed in the solution of sulfuric acid and zinc sulfate. A current was passed for a moment through this cell at a sufficient e.m.f. to deposit zinc. The circuit was then opened and the potential of the zinc cathode taken when it had reached a fairly constant value using a normal calomel electrode. The values secured from separate trials agreed within 2 millivolts. When the circuit was opened the potential quickly dropped a small amount and then remained constant for a time before appreciable action of the acid upon the metal took place; the potential during this

period of constancy was taken to be that of zinc in the solution in question. The value obtained was found to equal the back e.m.f. as shown by the commutator method, when zinc was being deposited at *very low current densities*. While the determination cannot be regarded as very exact, it was found to be sufficiently accurate for the work herein reported. In presenting the data which follow it has been found convenient in each case to express the zinc potential in terms of the hydrogen overvoltage corresponding to the same; i. e., the difference in volts between the potential of the zinc and that of the reversible hydrogen electrode.

It was found convenient, throughout the experiments, to employ a normal calomel electrode instead of a hydrogen electrode for measuring the cathode potentials, and separately to determine the hydrogen potential for the solution. The latter was accomplished with the use of the same calomel electrode; 2 hydrogen electrodes were used which gave identical results. From the data secured the difference between the various cathode potentials and that of the reversible hydrogen electrode (the overvoltage) was easily calculated. In all cases a saturated potassium chloride solution was employed to connect the 2 electrodes, to minimize any liquid-liquid potential. The unavoidable variations caused by changes in the electrode surface, time, etc., are, with both methods, of sufficient magnitude to overshadow completely corrections for liquid-liquid potential or small changes of temperature. The measurements were made at approximately 20°.

In the direct method, great care must be taken to ascertain the potential between the cathode surface and the electrolyte in immediate contact with it. To effect this, the solution connecting the standard electrode was connected with the experimental electrode by means of a capillary tube of about 1 mm. in diameter, the end of the capillary being not more than 0.2 mm. from the surface of the cathode. See B, Fig. 1.

To determine whether the direct method satisfies Requirement 1 mentioned above, an experiment was carried out using bright platinum electrodes in dil. sulfuric acid and measuring the cathode potential at constant current density but varying the distance between the electrodes. The results obtained are given in Table I.

TABLE I  
EFFECT OF ELECTRODE SPACING ON POTENTIAL MEASUREMENTS BY THE DIRECT METHOD  
Solution: dil. sulfuric acid

Current Amp.	Electrode spacing Cm.	Cathode potential, calomel electrode being taken as +0.56 volt Volts	Current Amp.	Electrode spacing Cm.	Cathode potential, calomel electrode being taken as +0.56 volt Volts
0.200	0.5	-0.654	0.200	15.0	-0.650
	15.0	-0.656		10.0	-0.371
	0.5	-0.656	0.800	8.0	-0.371
	15.0	-0.657		0.5	-0.3704
	0.5	-0.651			

The results show that changes as great as 30 times the cathode-anode

spacing did not appreciably alter the cathode potential, the current density remaining constant. However, moving the capillary away from the electrode surface greatly increased the potential reading. The size or shape of the containing vessel was found not to influence the results.

It appeared obvious that results obtained by the commutator method would be independent of the relative distances of the anode and cathode as well as of the position of the bridge connecting the cathode with the standard electrode, but this was verified by experiment.

Both methods of measurement having fulfilled the requirements of Requirement 1, the next step was to investigate the commutator method with a view of ascertaining its meeting Requirement 2. If the fall of potential is appreciable during the period of interruption, a variation in the value of the back e.m.f. with speed of rotation would naturally result. Approximately ten tests were made, all of which gave similar results, of which the following is a typical example.

Sulfuric acid, 0.527 *N*, containing 15 g. per liter of zinc as zinc sulfate, was electrolyzed, using an iron cathode. The current was gradually raised at intervals and the cathode potential determined by both methods. The speed of the commutator was varied from about 8 to 40 revolutions per second. The data are reported in Table II.

TABLE II  
EFFECT OF SPEED OF ROTATION OF COMMUTATOR ON OVERVOLTAGE READINGS  
Solution: 0.527 *N* sulfuric acid, containing 15 g. per liter of zinc as zinc sulfate  
Speed of commutator: 8 to 40 revolutions per second

Current density Amps. per sq. dcm.	Hydrogen overvoltage		Valuation with speed
	Commutator method	Direct method	
	Volts	Volts	Volts
0.13	0.255 to 0.256	0.321	0.001
0.63	0.210 to 0.365	0.433	0.155
2.55	0.765	0.870	None

At the highest potential given, zinc was being deposited instead of hydrogen. There was little or no variation in potential with speed of rotation of the commutator just prior to the first evolution of hydrogen or after the transition point was reached when the cathode had changed to a zinc surface. In the intervening period, however, when hydrogen gas was being given off, the variation was from 0.100 to 0.200 volts, the potential reading increasing with the commutator speed. This shows that in a circuit where molecular hydrogen is being formed the fall of potential at the electrode surface, during the period of interruption of the current, is considerable between the speeds given. When gas is being evolved, the difference between the two methods is greater than before the evolution of hydrogen or after the deposition of zinc, the direct method always giving the higher result.

Experiments were next made to ascertain the effect of current density on the divergence of the two methods. The electrolyte used was 0.5 *N* sulfuric acid. In each experiment the applied e.m.f. was gradually raised until the first continuous current was noted from the milli-ammeter. The current density was gradually raised at intervals of about 2 minutes and measurements made by both methods. The current was interrupted by the commutator only long enough to make the readings for this method. The average speed of rotation of the commutator was about 30 revolutions per second. The overvoltage data will be found in Table III. The greater the current density the greater is the difference in the values by the two methods, the commutator method always giving the lower result.

TABLE III  
COMPARISON OF OVERVOLTAGES BY THE TWO METHODS WITH INCREASING CURRENT DENSITIES

Solution: 0.5 <i>N</i> sulfuric acid								
Current density Amps. per sq. dcm.	Platinized platinum		Nickel		Cathode Metal Copper		Iron	
	Commu- tator method Volts	Direct method Volts	Commu- tator method Volts	Direct method Volts	Commu- tator method Volts	Direct method Volts	Commu- tator method Volts	Direct method Volts
0.13	...	...	0.204	0.235	0.440	0.518	...	...
0.26	0.011	0.011	0.238	0.312	0.456	0.563	0.248	0.290
0.39	0.010	0.015	0.235	0.324	0.454	0.619	0.297	0.431
0.51	...	...	0.239	0.346	0.463	0.664	0.312	0.494
0.64	0.015	0.020	0.240	0.356	0.475	0.690	0.354	0.584
0.77	...	...	0.254	0.373	0.480	0.719	0.330	0.643
0.89	...	...	0.261	0.387	0.485	0.770	0.351	0.698
1.02	...	...	0.259	0.413	0.475	0.775	0.325	0.751
1.27	0.018	0.022	0.275	0.432	0.475	0.832	...	...
2.55	0.020	0.028	0.314	0.519	0.475	0.912	...	...
3.82	...	...	0.327	0.560	...	...	...	...
5.10	0.018	0.035	0.332	0.607	0.440	1.066	...	...
10.20	0.021	0.047	0.330	0.691	0.440	1.145	...	...
19.10	0.026	0.067	0.345	0.940	0.430	1.213	...	...

Experiments were next conducted using a solution of the same hydrogen-ion concentration as 0.5 *N* sulfuric acid but containing 15 g. per liter of zinc in the form of zinc sulfate. The solution was 0.527 *N* with respect to the acid. Measurements were made similarly with increasing current density and the potentials noted as the transition point from hydrogen to zinc was reached. The zinc potential corresponded to an overvoltage of 0.758 volts. The values are recorded in Table IV.

The overvoltages for low current densities given in Table IV correspond to those of Table III. With time and increase of current density, however, the rise of cathode potential is more rapid in the case of the electrolyte containing zinc. A possible explanation of this result is that during the

TABLE IV

COMPARISON OF OVERVOLTAGES BY THE TWO METHODS USING SOLUTION CONTAINING SULFURIC ACID AND ZINC SULFATE

Solution: 0.527 *N* sulfuric acid, containing 15 g. per liter of zinc as zinc sulfate  
Zinc potential corresponds to overvoltage of 0.758 volts

Cathode Metal

Nickel			Copper			Iron		
Current density Amps. per sq. dcm.	Commu- tator method Volts	Direct method Volts	Current density Amps. per sq. dcm.	Commu- tator method Volts	Direct method Volts	Current density Amps. per sq. dcm.	Commu- tator method Volts	Direct method Volts
0.13	0.224	0.278	0.13	0.425	0.471	0.13	0.245	0.321
0.26	0.235	0.305	0.13	0.505	0.563	0.26	0.253	0.361
0.51	0.249	0.355	0.20	0.529	0.628	0.64	0.365	0.433
0.76	0.256	0.393	0.26	0.693	0.745	1.27	0.295	0.512
1.53	0.345	0.565	0.26	0.685	0.775	2.29	0.311-0.429	0.623
1.53	0.357	0.620	0.26	0.748	0.808	2.29	0.740	0.900
1.53	0.720	0.875	0.38	0.757	0.810	2.55	0.765	0.870
1.53	0.761	0.880	0.51	0.758	0.800	5.10	0.755	0.845
1.91	0.765	0.843	1.28	0.759	0.802	..	.....	...
3.82	0.771	0.875	5.10	0.758	0.802	..	.....	...
10.30	0.777	0.920	10.30	0.763	0.827	..	.....	...
19.10	0.775	0.950	19.10	0.668	0.854	..	.....	...

electrolysis there is an increase in the concentration of the zinc sulfate and a decrease of sulfuric acid at the cathode. This would be accompanied by a change in hydrogen-ion concentration and consequently of the hydrogen potential. The cathode potential in an acid solution containing zinc sulfate would therefore not be the same at a given current density as that in an acid solution having the same initial hydrogen-ion concentration.

The results indicate that the ordinary overvoltage tables, obtained with the use of pure acid solutions as the electrolyte, do not show the current densities necessary for the deposition from acid solutions of metals having a greater electromotive force than hydrogen.

The data of Table IV also show that the potential values obtained by the two methods of measurement became more and more divergent with increase in current density until, according to the direct method, the zinc potential was reached and zinc deposited. At this point the values obtained by the two methods approach each other closely, the values of the commutator method suddenly rising to practically that of the zinc potential. Upon reaching this critical point, the potential as measured by the direct method suddenly rose to a slightly higher value. This rise was only temporary, however, and gradually disappeared as the coating of zinc on the cathode became more uniform. In all cases it was found that at the critical potential for the deposition of metal there was a very abrupt change in the values obtained by the commutator method.

A further series of experiments was tried with the object in view of controlling any sudden rise in potential. To accomplish this the applied

e.m.f. was gradually decreased as the point for metal deposition was reached. Readings were made by both methods in quick succession at time intervals of about 1 minute. In the commutator method the current is flowing only intermittently and the time factor is therefore not parallel to that of the direct method. To avoid any influence of time on the overvoltage, the potential was read according to the direct method, then the potentiometer was set at the approximate value for the commutator reading, the commutator was suddenly connected in the circuit and the final reading taken as quickly as possible. This was done in order to obtain the readings by the two methods under conditions as nearly identical as was possible. Two electrolytes and two different metals were used; in one case, a nickel cathode was tried with the same solution as that referred to in Table IV; in the other case, bright platinum with a solution which was 0.204 *N* with respect to sulfuric acid and containing sufficient zinc sulfate to give 120 g. of zinc per liter, as zinc sulfate. The zinc potential with the latter solution was equivalent to an overvoltage of 0.708 volts. Representative results will be found in Table V. Only the last part of each series of readings is given; those of the first part correspond to the values given in Table IV.

TABLE V

COMPARISON OF OVERVOLTAGES BY THE TWO METHODS WITH GRADUAL POTENTIAL RISE  
Solution used with nickel cathode: 0.527 *N* sulfuric acid containing 15 g. per liter of zinc as zinc sulfate

Zinc potential: overvoltage of 0.758 volts

Solution used with bright platinum cathode: 0.204 *N* sulfuric acid, containing 120 g. per liter of zinc as zinc sulfate

Zinc potential: overvoltage of 0.708 volts.

Nickel			Bright Platinum		
Current density Amps. per sq. dc.	Commutator method Volts	Direct method Volts	Current density Amps. per sq. dc.	Commutator method Volts	Direct method Volts
0.64	0.338	0.675	0.38	0.247	0.697
0.13	0.323	0.705	0.38	0.250	0.712
0.26	0.320	0.735	0.26	0.682	0.737
0.13	0.322	0.755	0.13	0.695	0.747
0.07	0.675	0.765	0.13	0.693	0.777
0.07	0.700	0.765	0.33	0.702	0.797
..	...	...	0.77	0.719	0.817

The direct method shows a *gradual increase* in potential without any sudden changes or fluctuations, and zinc was deposited upon reaching the zinc potential. When the zinc potential was registered by the direct method, there was a sudden and abrupt rise in the commutator readings. This sudden break is shown with both solutions although these had distinctly different zinc potentials.

Attempts were also made using the commutator arrangement by itself

to increase the potential *gradually* to the point for metal deposition without any sudden change in the magnitude of the readings. The commutator rotated at the rate of 30 revolutions per second. The electrolyte was the same as that used for obtaining the results given in Table IV. Using an iron cathode, as soon as the potential had been raised by steps to an overvoltage of 0.460, the readings immediately rose to 0.758, the value of the zinc potential, and zinc began to deposit. By lowering the applied e.m.f. until the thin coating of zinc dissolved, the overvoltage remained at 0.745 and then suddenly became less than 0.375. There was no point between 0.460 and 0.758 at which the potential could be held, in spite of numerous trials. Similar results were obtained with cathodes of bright platinum and nickel. The phenomenon of the abrupt change in readings is typical of the commutator method using cathodes of metal of low overvoltage in acid solutions of zinc sulfate.

The preceding tabulated data were secured with a limited number of solutions. Analogous results have been obtained with other solutions in which the concentrations of both sulfuric acid and zinc sulfate were varied, thus giving different values for the hydrogen and zinc potentials. *The sudden break in the commutator readings has been found to be not characteristic of a given potential nor of the nature of the cathode metal, but is determined by the zinc potential.*

### Discussion of Results

The experimental data presented above show that more consistent results are obtained by the direct method. The sudden and abrupt changes in the readings with the commutator method given in Tables IV and V furnish practically decisive evidence that this method cannot be relied upon to give the true overvoltage. There is no experimental evidence reported in the literature to show that the counter e.m.f. is instantaneously constant when the current is interrupted and has the same value as when the exciting current is flowing. The foregoing data furnish strong evidence to the contrary. The hydrogen overvoltage must be sufficient for the cathode to reach the zinc potential before zinc is deposited. Evidently this point would be reached gradually. A method for determining overvoltage must show this gradual change of potential and at the critical point for metal deposition must closely coincide with the zinc potential. The direct method meets this requirement.

The data of Table III show that there was no abrupt rise in the overvoltages by the commutator method even when the values by the direct method were greater than those at which this sudden change was found in the experiments of Table IV. The values in Table III by the commutator method would indicate that, at the current densities used, it would be impossible with the metals employed to reach a cathode potential at which



zinc would be deposited. Nevertheless, it is an experimental fact that zinc can be deposited from an acid solution of the same hydrogen-ion concentration and within the same range of current density (See Table IV).

Consideration will now be given to Requirement 2 mentioned previously. While overvoltage is generally accepted to represent a potential, the difference in the results by the two methods of measurement has been taken to be due to a resistance, commonly designated as "transfer resistance."<sup>2</sup> The experimental work here presented shows the commutator method to be in error and consequently the so-called transfer resistance cannot be of the magnitude which has been claimed.<sup>3</sup> The data also show that the measurements made by the direct method do not vary in any case from the zinc potential at the point of zinc deposition by more than 0.05 volts. With a smooth electrode surface such as that afforded by bright platinum and with careful control of the rise in potential, zinc was deposited at 0.029 volts above the zinc potential, when the current density was 0.0026 amperes per sq. cm. This would represent a transfer resistance of approximately 11 ohms. By further refinement of the method of procedure it might be possible to show the non-existence of a resistance of even this magnitude. These results, considered with the comments recently made by MacInnes,<sup>3</sup> based upon more precise measurements, show that the probable error in the direct method due to the presence of a resistance at the electrode surface is of small proportion, if it exists at all.

In conclusion the writers wish to express their sincere thanks to Dr. D. A. MacInnes, of the Massachusetts Institute of Technology, who has read this paper in manuscript and given useful suggestions.

### Summary

1. The findings of former investigators that overvoltage increases with time and current density and varies with the nature of the electrode surface has been confirmed.

2. A comparison, based upon the transition point for hydrogen-zinc deposition from solutions containing sulfuric acid and zinc sulfate, has been made of the two methods used for overvoltage measurement. The data obtained show that the commutator method gives erroneous results; when gas is being evolved at the experimental electrode the error is large and varies with the speed of rotation of the commutator. The direct method has been found to give more consistent results and to be the more accurate method; the criticism that it is subject to variation due to electrode spacing and size and shape of containing vessel has been shown to be invalid.

3. The existence of an appreciable transfer resistance at the surface of

<sup>2</sup> Newbery, *Trans. Faraday Soc.*, 19, 126 (1919).

<sup>3</sup> MacInnes, *THIS JOURNAL*, 42, 2233 (1920).

the electrodes studied is doubtful. While gas is being evolved it is evidently not of the magnitude which has been claimed.

4. Evidence has been secured which indicates that the ordinary hydrogen overvoltage tables, obtained by using pure acid solutions as the electrolyte, do not show the current densities necessary for the deposition from acid solutions of metals having a greater electromotive force than hydrogen.

SEATTLE, WASHINGTON

## THE SOLUBILITY OF ALUMINUM NITRATE CRYSTALS IN SOLUTIONS OF NITRIC ACID OF VARIOUS STRENGTHS AT VARIOUS TEMPERATURES

BY LOWELL H. MILLIGAN

Received December 20, 1921

In connection with other work which was in progress, it was necessary to determine the solubility of aluminum nitrate crystals,  $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ , in solutions of nitric acid of various strengths, at various temperatures. The results obtained seem to be of sufficient general interest to warrant publication.

The literature fails to reveal any quantitative data on the solubility of this substance  $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ . Seidell<sup>1</sup> gives no data whatsoever. Comey<sup>2</sup> states: "Deliquescent. Very soluble in  $\text{H}_2\text{O}$ ,  $\text{HNO}_3$  + Aq, or alcohol. (Berzelius)." Probably the best bibliography on aluminum nitrates is found in Friend's "A Text Book of Inorganic Chemistry"<sup>3</sup> In addition to the references there, Inamura<sup>4</sup> has made a phase rule study of the system aluminum nitrate:water:nitric acid, at  $25^\circ$  and finds that the nonhydrate is the stable hydrate in the presence of nitric acid of less than 73% strength.

Preliminary experiments showed that the sirupy filtered liquor resulting from digestion of nitric acid with an excess of aluminum hydroxide was slow to crystallize, and the crystals formed from it were very small and difficult to filter. Because of this behavior of solutions containing no free nitric acid, it is perfectly possible to obtain a sirupy liquor which is more or less stable at room temperature with respect to aluminum nitrate nonhydrate and contains less water than the crystals of this hydrate. On standing for a few days such a liquor will become cloudy and deposit a white substance which is probably a basic salt. When, however, nitric

<sup>1</sup> Seidell, "Solubilities of Inorganic and Organic Compounds," D. Van Nostrand Co., 1919.

<sup>2</sup> Comey, "A Dictionary of Chemical Solubilities," MacMillan and Co., 1896, p. 243.

<sup>3</sup> "A Textbook of Inorganic Chemistry," Ed. J. N. Friend, Chas. Griffin and Co., Ltd., 1917, vol. IV, p. 88.

<sup>4</sup> Inamura, *J. Tokyo Chem. Soc.*, 41, 1 (1920), through *C. A.*, 14, 2451 (1920).

acid is added to this liquor, rapid crystallization takes place with the formation of colorless coarsely-granular crystals of the nonahydrate. The following study of the solubility of these crystals in solutions of nitric acid of various strengths, at various temperatures, was made to obtain quantitative data on this phenomenon.

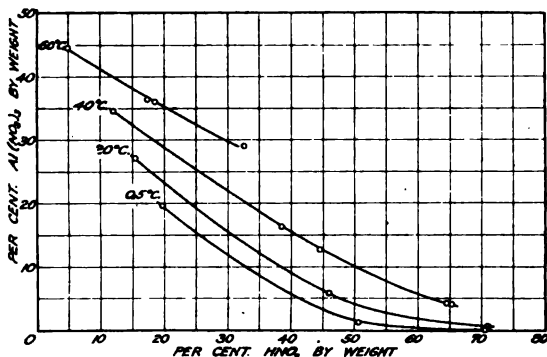


Fig. 1.—The solubility of  $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  in nitric acid of various strengths, at various temperatures.

Aluminum nitrate crystals were prepared by dissolving pure washed aluminum hydroxide, obtained by cooling a hot conc. solution of sodium aluminate, in c. p. nitric acid. The resulting solution, which contained an excess of nitric acid, was cooled and the crystals which separated were centrifuged until dry, and then bottled and analyzed.

#### ANALYSES\*

	Found %	Calc. for $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ %
$\text{Al}_2\text{O}_3$ .....	13.45	13.61
$\text{NO}_3$ (titration) .....	49.4	49.57
$\text{SiO}_2$ .....	None	.....
$\text{TiO}_2$ .....	None	.....
$\text{Fe}_2\text{O}_3$ .....	0.012	.....

\* The sodium in these crystals was not determined, but it must have been very low because the aluminum hydroxide from which the original solution was made contained only 0.05% of  $\text{Na}_2\text{O}$ .

An excess of these crystals was put in a large test-tube and covered with nitric acid of the desired strength. The tube, which was fitted with a rapidly rotating stirrer, was then placed in a thermostat. After about 30 minutes the stirring was stopped for about 5 minutes and a sample of the clear liquor rapidly pipetted into a weighing bottle which was stoppered and weighed when it had reached room temperature. The sample was diluted to a given volume and aliquots were analyzed gravimetrically for alumina by precipitation with ammonia, and volumetrically for total nitrate by titration in a boiling solution with standard

sodium hydroxide solution and phenolphthalein as indicator.<sup>5</sup> The alumina was calculated to aluminum nitrate  $\text{Al}(\text{NO}_3)_3$ , and the residual nitrate over that required to combine with the aluminum, to nitric acid  $\text{HNO}_3$ . These constituents were expressed as grams per 100 grams of the original solution.

TABLE I  
THE SOLUBILITY OF  $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  IN NITRIC ACID OF VARIOUS STRENGTHS, AT  
VARIOUS TEMPERATURES

No.	Temp. ° C.	Approximate Sp. Gr. of Soln. Indicated temp./20°	$\text{HNO}_3$ % by wt.	$\text{Al}(\text{NO}_3)_3$ % by wt.
1-a	0.4	1.311	20.6	19.1
b	0.4	1.311	18.9	20.2
2-a	0.5	1.335	51.3	1.54
b	0.5	1.336	50.0	1.46
3-a	0.5	1.433	72.4	0.25
b	0.5	1.431	68.9	0.21
4-a	19.8	1.351	15.4	27.2
b	19.8	1.349	15.5	27.0
5-a	20.0	1.339	46.8	5.88
b	20.0	1.341	45.3	5.83
6-a	20.0	1.415	71.4	0.67
b	20.0	1.415	71.3	0.79
7-a	40.0	1.400	11.6	34.6
b	40.0	1.398	12.3	34.6
8-a	40.0	1.374	38.6	16.3
b	40.0	1.367	38.4	16.3
9-a	40.0	1.375	44.7	12.9
b	40.0	1.373	44.9	13.2
10-a	40.0	1.410	64.7	4.17
b	40.0	1.408	64.3	4.13
11-a	40.0	1.398	65.4	4.09
b	40.0	1.401	65.3	4.18
12-a	60.0	1.457	4.98	44.3
b	60.0	1.460	4.88	44.4
13-a	60.0	1.457	16.7	37.0
b	60.0	1.461	17.6	35.8
14-a	60.0	.....	18.8	36.2
b	60.0	1.450	19.0	35.8
15-a	60.0	1.461	32.8	29.3
b	60.0	1.462	32.5	28.9

After the first sample had been taken, the stirrer was started again, and in a few minutes another sample of the solution was withdrawn and the analysis averaged with that of the first sample to give a point on the solubility curve. The results of these experiments are given in Table I, and the averages have been plotted as curves in Fig. 1. A 10cc. pipet was used to measure out the liquid, and consequently it was an easy

<sup>5</sup> See Scott, "Standard Methods of Chemical Analysis," D. Van Nostrand Co., 1920, p. 11. The method is there described for  $\text{Al}_2(\text{SO}_4)_3$ .

matter to compute the approximate specific gravity of the liquor samples at the indicated temperature of the experiment compared with water at 20°; this information is given in the third column of the table.

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ITHACA, NEW YORK

[CONTRIBUTION FROM THE COBB CHEMICAL LABORATORY OF THE UNIVERSITY OF VIRGINIA]

## THE FACTORS DETERMINING THE HYGROSCOPIC PROPERTIES OF SOLUBLE SUBSTANCES. I. THE VAPOR PRESSURES OF SATURATED SOLUTIONS

BY GRAHAM EDGAR AND W. O. SWAN<sup>1</sup>

Received December 26, 1921

### Introduction

A dry, crystalline, water-soluble solid, not forming a crystalline hydrate, will, when exposed to air containing water vapor, tend to absorb moisture, with the formation of a saturated solution. If we neglect for the moment pure surface adsorption, such absorption can occur only when the vapor pressure of the saturated solution is lower than the partial pressure of water vapor in the atmosphere to which the solid is exposed. Since the vapor pressure of any aqueous solution is lower than that of pure water, any solid will absorb moisture when exposed to *saturated* aqueous vapor, and is therefore to some extent "hygroscopic." This term, however, is commonly applied only to such substances as absorb moisture readily from air under normal atmospheric conditions.

Although the hygroscopic properties of commercial solids which are to be sold in other than sealed containers (for example, fertilizer salts) play an important part in limiting the commercial applications of such solids, no careful scientific study seems to have been made of the factors involved in determining the extent or rate of their absorption of moisture.

As indicated above, the vapor pressure of the saturated aqueous solution determines the partial pressure of water vapor with which the solid (and its saturated solution) may be in equilibrium; a solid may be expected to absorb moisture when exposed to an atmosphere containing more water vapor than this, and conversely the moist solid will lose water when exposed to an atmosphere containing a lower partial pressure of water vapor. The *rate* at which the moisture will be absorbed will depend upon a number of factors. We can predict from *a priori* considerations that the rate of moisture absorption will be affected by (1) the difference between the partial pressure of water vapor in the atmosphere and the

<sup>1</sup> Certain preliminary measurements were made by N. E. Oglesby

vapor pressure of the saturated aqueous solution ( $P_{H_2O} - P_{\text{sat. sol.}}$ ), (2) the temperature, (3) the surface of solid exposed, (4) the velocity of movement of the moist air, and (5) a specific "reaction constant," characteristic of the solid itself.

The present research represents an attempt to analyze as completely as may be possible the influence of the separate factors in determining the hygroscopic properties of typical water-soluble solids not forming crystalline hydrates. The substances selected for investigation were potassium, sodium and ammonium nitrates, potassium and ammonium chlorides, ammonium sulfate and dihydrogen orthophosphate, and urea. A mixture of potassium nitrate and ammonium chloride has also been studied. The selection was made to include substances of various degrees of solubility and of different chemical types. All of the substances studied have also a certain commercial interest.

Part 1 deals entirely with the measurement of the vapor pressures of the saturated aqueous solutions.

### Previous Data

While large numbers of vapor-pressure measurements are recorded in the literature, very few data at all reliable are available upon the saturated aqueous solutions of the substances in question at low temperatures (20–30°).

Speranski<sup>2</sup> measured the vapor pressures of saturated aqueous solutions of potassium and sodium nitrates and potassium chloride, using the Bremer-Frowein tensimeter. His results will be discussed below.

Hartung<sup>3</sup> measured the vapor pressure of a saturated solution of potassium chloride, obtaining results not in good agreement with those of Speranski.

Lovelace, Frazer and Sease<sup>4</sup> made very careful measurements of the vapor pressure of potassium chloride solutions of different concentrations at 20°. By a very short extrapolation of their data the value for the saturated solution may be calculated.

Lincoln and Klein<sup>5</sup> measured the vapor pressures at 25° of sodium nitrate solutions sufficiently concentrated to permit extrapolation to the saturation value with reasonable confidence.

Measurements upon less concentrated solutions of a few of the substances in question<sup>6</sup> may be extrapolated to the saturation point, but in most cases this extrapolation must be carried too far to be reliable.

Lescœur<sup>7</sup> measured the vapor pressures of the saturated solutions of a number of salts, but his values are in marked disagreement with those of all other investigators and are frequently in obvious error.

In view of the paucity of data and the lack of concordance in such data as exist, it was determined to measure the vapor pressures of satu-

<sup>2</sup> Speranski, *Z. physik. Chem.*, **70**, 519 (1910) and **78**, 86 (1912).

<sup>3</sup> Hartung, *Trans. Faraday Soc.*, **15**, [III] 150 (1920).

<sup>4</sup> Lovelace, Frazer and Sease, *THIS JOURNAL*, **43**, 102 (1921).

<sup>5</sup> Lincoln and Klein, *J. Phys. Chem.*, **11**, 318 (1907).

<sup>6</sup> Landolt-Börnstein "Tabellen."

<sup>7</sup> Lescœur, *Ann. chim.*, [VII] **7**, 416 (1896).

rated aqueous solutions of the substances listed above at temperatures representing normal atmospheric conditions, namely 20–30°.

### Experimental Methods

After consideration of several possible methods, that proposed by Smith and Menzies<sup>8</sup> employing the isoteniscope, was selected. The apparatus and experimental technique were essentially those of Smith and Menzies, except for minor modifications.

The bulb of the isoteniscope was enlarged to contain about 15 cc., and a small trap was sealed in above it to guard against loss from the "bumping" which sometimes occurred. A heavy mineral oil, possessing no appreciable vapor pressure, was used as confining liquid, following the procedure of Derby and Yngve.<sup>9</sup> The isoteniscope was connected to a 10-liter bottle as balancing reservoir, which in turn was connected to a 3-stage Cenco-Nelson pump, a manometer, and a side tube through which air could be admitted. The isoteniscope was maintained at constant temperature by immersion in an air-jacketed glass vessel of water, heated by a coil of glass tubing through which warm water could be circulated, and vigorously stirred by a turbine stirrer.

The thermometer used could be read to 0.01°, and had been compared with one calibrated by the Bureau of Standards. The manometer was of the closed type, constructed from 16-mm. Pyrex tubing (to minimize meniscus errors), and filled with carefully purified mercury. It was repeatedly boiled out to remove air. A glass scale, which had been compared with a standard meter, was placed directly behind the mercury column. Readings were made by means of a cathetometer, placed about a meter away, the millimeters being read directly from the glass scale, and the fractions estimated by means of the micrometer screw of the cathetometer, which permitted estimation to 0.01 mm. The manometer was tapped continuously to avoid "sticking" of the mercury. All readings were reduced to millimeters of mercury, at 0°.

In carrying out a determination the procedure was as follows.

The bulb of the isoteniscope was filled about  $\frac{2}{3}$  full of a mixture of the solid and water, a sufficient excess of solid being added to occupy about half of this volume. The bulb was then sealed to the rest of the apparatus, the pump started, and the apparatus evacuated until the contents of the bulb boiled vigorously. After the boiling had continued for some time the pump was shut off, and air was admitted into the large bottle until the oil in the leveling tube showed no pressure difference between the bulb and the air reservoir. The manometer was then read and the process of boiling out repeated until 3 to 10 concordant readings had been obtained. Throughout the entire procedure the bulb was vigorously agitated. The temperature was then changed and the process repeated. Usually in making a series of determinations at different temperatures, measurements obtained at rising temperatures were repeated at falling temperatures to make sure that errors due to failure to achieve saturation of the solution might be detected.

<sup>8</sup> Smith and Menzies, *THIS JOURNAL*, **32**, 1921 (1910).

<sup>9</sup> Derby and Yngve, *ibid.*, **38**, 1439 (1916).

TABLE III  
COMPARISON OF DATA

1 Solid	2 Temp. °C.	3 V. p. Mm.	Ref.	4 V. p. Mm. (E. and S.)
NH <sub>4</sub> NO <sub>3</sub>	20.0	9.1	7	11.15
	23.8	16.47	11	16.49
NaNO <sub>3</sub>	25.8	18.57	11	18.51
	27.8	20.66	11	20.74
	25.0	17.64	12	17.69
	23.2	18.77	11	18.27
	26.3	22.32	11	21.70
KCl	29.34	26.14	11	25.87
	30.01	26.62	3	26.85
	20.00	14.96	4	14.97
KNO <sub>3</sub>	20.0	16.7	13	16.58
	28.63	27.24	11	27.58

The data for potassium chloride are uniformly lower than those of Speranski; the value at 30° is somewhat higher than that of Hartung, while the value at 20° is in complete agreement with the extrapolated value from the careful measurements of Lovelace, Frazer, and Sease.

The value for potassium nitrate at 28.63° is higher than Speranski's single measurement, but that at 20° is in fair agreement with the extrapolated data from Landolt-Börnstein "Tabellen."

Altogether there seems no reason to doubt that the data are very close to the correct values.

It should be noted that, as is to be expected, the vapor pressures of the solutions saturated with both ammonium chloride and potassium nitrate are considerably lower than those of solutions saturated with either constituent alone. The bearing of this fact upon the hygroscopic properties of mixtures will be pointed out in a later communication.

### Theoretical Considerations

For solutions as concentrated as those involved in the present investigation it is not to be expected that any simple law will express accurately a relation between the vapor pressure and the temperature and solubility of the solid.

Various empirical interpolation formulas, to express the variation of the vapor pressure of saturated solutions with the temperature, have been proposed by Speranski<sup>2</sup> but it seems hardly worth while to consider their application to a temperature range as limited as that of the present investigation.

<sup>11</sup> Speranski, Ref. 2, corrected by the use of the data of Scheele and Heuse, Ref. 10, for pure water.

<sup>12</sup> Lincoln and Klein, Ref. 5, extrapolated.

<sup>13</sup> Landolt-Börnstein "Tabellen," 4th Ed.



From the standpoint of general theory the following may be of interest.

If we neglect the volume of the solution in comparison with that of the solvent vapor, and assume that the vapor obeys the gas laws, the Clausius-Clapeyron equation becomes

$$\frac{d(\ln P)}{dT} = \frac{Q}{RT^2} \quad (1)$$

where  $Q$  is equal to the net heat effect accompanying the evaporation of 1 mol of solvent vapor and the precipitation of that quantity of solute dissolved in 1 mol of solvent.  $Q$  is evidently equivalent to the heat of combination of one mol of solvent *vapor* with that quantity of solid sufficient to form a saturated solution, and may thus be regarded as equal to  $Q_1 - SQ_2$ , where  $Q_1$  is the heat of evaporation of 1 mol of pure solvent,  $S$  the number of formula weights of solute dissolving in one mol of solvent, and  $Q_2$  the "integral" heat of solution of one formula weight of solute in the pure solvent.

Since we also have, from Van't Hoff<sup>14</sup>

$$Q_2 = RT^2 i \frac{(d \ln i S)}{(dT)} \quad (2)$$

where  $i$  is a factor expressing the deviation of the solution from the laws of ideal solutions, if we place  $Q = Q_1 - SQ_2$ , and combine Equations 1 and 2, we obtain

$$\frac{d(\ln P)}{dT} = \frac{Q_1}{RT^2} - \frac{i S d(\ln i S)}{dT} \quad (3)$$

whence

$$\frac{d(\ln P)}{dT} = \frac{Q_1}{RT^2} - \frac{d(i S)}{dT} \quad (4)$$

or

$$\frac{d(i S + \ln P)}{dT} = \frac{Q_1}{RT^2} \quad (5)$$

As an approximation we may assume both  $Q_1$  and  $i$  to be constant for a limited temperature range, and on integration we obtain

$$\ln P_1 - \ln P_2 = i (S_2 - S_1) - \frac{Q_1}{R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right) \quad (6)$$

For concentrated solutions of the type presented in this paper the values of  $i$  may perhaps best be obtained by substituting two experimental values for  $P_1$  and  $P_2$ . If this is done, the vapor pressures calculated from equation (6) for intermediate temperatures are in good agreement with our experimental results.

<sup>14</sup> See Noyes and Sammet, *Z. physik. Chem.*, **43**, 513 (1903).

### Summary

1. The vapor pressures of saturated aqueous solutions of potassium chloride, potassium nitrate, ammonium chloride, ammonium sulfate, ammonium nitrate, ammonium dihydrogen orthophosphate, sodium nitrate, urea, and a mixture of ammonium chloride and potassium nitrate have been measured at temperatures between 20° and 30°.

2. The relation of the vapor pressures of saturated aqueous solutions to the hygroscopic properties of soluble substances has been briefly discussed.

3. The theory relating the vapor pressure of a saturated solution to the temperature and solubility of the solid has been indicated.

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[CONTRIBUTION FROM THE T. JEFFERSON COOLIDGE, JR., CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

## THE PURITY OF ATOMIC WEIGHT SILVER. I. GASES IN PURE SILVER AND IODINE

BY GREGORY PAUL BAXTER AND LEON WOODMAN PARSONS

Received December 28, 1921

In a series of articles published in 1916 and subsequent years<sup>1</sup> entitled "Contributions to the Study of Sources of Error Affecting the Determinations of Atomic Weights," Ph. A. Guye and his collaborators have discussed critically and in much detail the various sorts of experimental evidence upon which atomic weight ratios depend. The most important sources of error to which attention is drawn are those resulting from impurities in the substances weighed. Under this head special emphasis is laid upon (1) gaseous impurities included in the interior of solids, (2) gaseous impurities condensed on the surfaces of solids, and (3) solid impurities.

Since metallic silver is a very important reference substance in the gravimetric determination of combining proportions, this substance has received especial attention at the hands of the Swiss scientists, and on the basis of experimental evidence doubt has been thrown on the purity of the silver which has served in the past as the standard of comparison. Unfortunately the evidence upon which the speculations of Professor Guye have been based has been obtained almost entirely from material the purification of which, if any, was far less complete than is essential in the most accurate work. It is much to be regretted, therefore, that, although realizing the desirability of repeating his own experiments using

<sup>1</sup> Guye, *J. chim. phys.*, 14, 25, 55, 83, 195, 204 (1916); 15, 360, 405 (1917); 16, 46 (1918).

the best material, he has seen fit to place great emphasis upon the necessity for corrections<sup>2</sup> of a highly questionable nature and magnitude.

The three suggestions mentioned above are by no means novel. All three sources of error have in the past repeatedly been the subjects of investigation both in the Harvard chemical laboratories and elsewhere. So far as silver is concerned, in general the evidence obtained has led to the conclusion that the proportion of impurities in the best material is too small to have an appreciable effect on the results.<sup>3</sup> Nevertheless, in view of the importance of the question, the subject has been further studied. The outcome of our study confirms the earlier conclusion that the best metallic silver, while in the strictest sense not chemically pure, does not contain sufficient impurity to affect the result of the most accurate work within the limit of experimental error.

The first subject to be investigated was the possible gas content of silver and iodine. In a recent paper by Guye and Germann<sup>4</sup> a method for the analysis of very small quantities of gas<sup>5</sup> has been applied to the analysis of gases disengaged from iodine during sublimation in a vacuum, and from silver by conversion to silver iodide in a vacuum. In a single experiment with 3 g. of iodine they obtained 30 mm.<sup>4</sup> of gas which, on the assumption that it has the density of air, represents 0.0013% of the weight of the iodine. They performed five experiments with silver. In three, metal of 99.8% purity was used without preliminary treatment. In two, a purer specimen<sup>6</sup> was fused in a quartz test-tube in a current of pure dry hydrogen which was bubbled through the molten metal for some time in order to sweep out gases. The less pure material was found to contain about 170 cu. mm. of gas per gram,  $\frac{4}{5}$  of which was oxygen and  $\frac{1}{5}$  carbon monoxide. The purer silver proved to be almost entirely free from oxygen but to contain 27 cu. mm. of carbon monoxide and 10 cu. mm. of water vapor per gram. Converted to percentages by weight these figures represent 0.0034% of carbon monoxide and 0.0008% of water, a total of 0.0042%. In another experiment<sup>7</sup> in which silver wire which had been heated in a vacuum was converted to chloride by means of chlorine, evidence was obtained that the gas content of the metal was greater in the inner than in the outer layers of the wire.

On the basis of these results Guye and Germann<sup>8</sup> make a preliminary

<sup>2</sup> See in particular, Guye and Germann, *J. chim. phys.*, **14**, 229 (1916). Guye, *ibid.*, **15**, 549 (1917).

<sup>3</sup> Richards and Wells, *Carnegie Inst. Pub.*, **28**, 16 (1905). *THIS JOURNAL*, **27**, 459 (1905).

<sup>4</sup> Guye and Germann, *Compt. rend.*, **159**, 225 (1914); *J. chim. phys.*, **14**, 204 (1916).

<sup>5</sup> *Compt. rend.*, **159**, 154 (1914); *J. chim. phys.*, **14**, 195 (1916).

<sup>6</sup> "Extra-pur a 1000/1000." Both samples were provided by the Société gènevoise de dégrossage d'or.

<sup>7</sup> *J. chim. phys.*, **14**, 227 (1916).

<sup>8</sup> *Compt. rend.*, **159**, 992 (1914); Ref. 2.

calculation of the effect of this gas upon the atomic weights of silver and of other elements which have been referred to silver, and find that while the effect upon the atomic weight of silver is small,  $-0.0045$  unit, the effect upon those of other elements may amount to several hundredths of a unit, *e. g.*,  $+0.005$  in the case of chlorine,  $-0.031$  in the case of tin.

The original investigation by Guye and Germann is an interesting one, although the outcome is not surprising in view of the questionable quality of the material examined. Certainly the matter is one demanding investigation. Under the circumstances we felt warranted in preferring to carry out this investigation ourselves, rather than to subject our material to Professor Guye for examination.

In outline we have followed closely the method of analysis used by Guye and Germann.<sup>9</sup> So far as possible we have examined material remaining from atomic weight researches. While it was impossible to investigate every specimen of iodine and silver which has been used in the past, a considerable variety of samples was available, and, since the specimens still remaining have already been compared with many others, there can be little question that the ground has been sufficiently covered.

### Purification of Iodine and Silver

**Iodine.**—Of the different samples of iodine examined in the course of the work, one consisted of commercial material which had merely been resublimed in a current of pure dry air, in a hard glass tube constricted at 3 points. The iodine was sublimed from porcelain boats into the portion of the tube included between the first 2 constrictions, where it was first melted to liberate moisture, and then sublimed into the next compartment where the process of melting and subliming was repeated. Finally, the product was sublimed a fourth time from the tube into a hard glass receiver from which it was transferred to the quartz tube. This sample (A) was prepared in an identical fashion for Expts. 3 and 5 (Table II).

A second sample of iodine was prepared by Baxter and Grose<sup>10</sup> for work upon the vapor pressure of iodine, and by Baxter and Harris<sup>11</sup> for an investigation on the atomic weight of arsenic. This material was distilled from aqueous potassium iodide and reduced to hydriodic acid by treatment with hydrogen sulfide under water. A possible impurity of cyanogen was eliminated as hydrocyanic acid by prolonged boiling of the solution and, after removal of sulfur by filtration, potassium permanganate was added and the iodine liberated was distilled from the residual solution of potassium and manganous iodides. A second reduction with hydrogen sulfide and oxidation of the hydriodic acid followed, and the

<sup>9</sup> This is a modification of that used by Guichard. *Compt. rend.*, 153, 272 (1911).

<sup>10</sup> Baxter and Grose, *THIS JOURNAL*, 37, 1061 (1915).

<sup>11</sup> Not yet published.

final product, after being rinsed, was dried over sulfuric acid. This sample is designated Sample B. An essentially similar method was used by Baxter<sup>12</sup> in earlier work upon the atomic weight of iodine, so that this specimen represents closely one sample of material involved in the question under discussion. Preparatory to examination for gaseous impurity it was sublimed in the manner already described (Expts. 1, 2 and 6) and part of the material was subjected to a second series of sublimations in exactly the same way (Expt. 4). The second series of sublimations apparently was without effect.

A third sample of iodine was made from iodic acid by first dehydrating the acid to the pentoxide and then decomposing the pentoxide into iodine and oxygen at a high temperature. This method also was used by Baxter.<sup>13</sup> One specimen of iodic acid had been made by Mr. P. C. Voter by acting on iodine with fuming nitric acid, and fractionally crystallizing the product many times. Since the material remaining consisted of fractions of intermediate purity, the fractional crystallization was continued for three more series of fractions. Although this material had been prepared and crystallized in quartz vessels, this point is of minor significance for the present purpose. The powdered crystals were carefully dehydrated in a current of pure dry air at gradually increasing temperatures up to 275°. Finally, the hard glass tube which had been used during the dehydration was heated until decomposition of the pentoxide took place, the iodine first being condensed and then thrice sublimed through the series of compartments of the tube as described above. The product was again sublimed through the hard glass tube before use (Sample C). The material used in Expt. 10 consisted of that used in Expts. 7, 8 and 9 after further sublimation in air. The material used in Expt. 17 was subjected to three series of sublimations in a quartz tube, the vapors passing over a roll of incandescent platinum gauze once in each series as described under Sample D. In Expt. 11 it is probable but not certain that Sample C was used.

Sample D of iodine was made from iodic acid prepared from potassium iodate through the barium salt, and subjected to a series of fractional crystallizations. This material also had been used by Baxter<sup>13</sup> in finding the ratio of silver to iodine. In Expt. 12 it was converted to iodine as described above. In Expts. 13 and 14 a quartz decomposition and sublimation tube was employed and the first constriction in the tube was filled with platinum gauze heated to redness. This served to decompose any iodine pentoxide which might have been blown along in the current of gas and also to facilitate the oxidation of the vapors of organic substances

<sup>12</sup> Baxter, *Proc. Am. Acad.*, **40**, 419 (1904); **41**, 73 (1905); *THIS JOURNAL*, **26**, 1577 (1904); **27**, 876 (1905); **32**, 1591 (1910).

<sup>13</sup> Baxter, *THIS JOURNAL*, **32**, 1591 (1910).

which may have been present. Baxter<sup>13</sup> used this same precaution. Before testing for gases this iodine was twice more sublimed through the silica tube (Sample D).

For Expts. 15 and 16 the iodine used in Expts. 12, 13 and 14 was twice sublimed in air through the silica tube with the incandescent platinum gauze. The iodine used in Expt. 18 was a mixture of residues from earlier experiments which was thrice sublimed through the silica tube containing the hot platinum gauze.

For purposes of comparison the treatment given iodine preparatory to weighing by Baxter in work on the atomic weight of iodine is summarized here. In the first investigation<sup>14</sup> carefully purified iodine was sublimed once from a crystallizing dish to a cool surface, and once from a hard glass tube into the weighing tube in a current of dry air. In the second investigation<sup>15</sup> the iodine was sublimed from one part of the hard glass sublimation tube to another and then again into the weighing tube, all in a current of pure dry air. In the third investigation<sup>16</sup> iodine pentoxide was decomposed at about 350° in a current of dry air. Then the iodine was fused, and finally was sublimed into the weighing tube and again fused. Another specimen was made in the same way in a quartz tube, but the iodine vapor was passed through hot platinum gauze. Still a third specimen of iodine which had been carefully purified in another way was twice sublimed in the quartz tube, once through the platinum gauze, and then a third time into the weighing tube where it was fused.

The material designated Sample D in this paper resembles most closely that used by Baxter in the latest and most satisfactory determinations of the ratio of silver to iodine, in that it was made from iodine pentoxide, was sublimed through platinum gauze in a current of air and oxygen, and was fused. The material used by Baxter had, however, been subjected to fewer sublimations than Sample D.

**Silver.**—All the silver examined consisted of specimens of material which had already been employed in determining atomic weight ratios. One group of samples had been prepared in a similar way by Baxter, Moore and Boylston,<sup>17</sup> Baxter and Grover,<sup>18</sup> and Baxter.<sup>19</sup> After an elaborate preliminary purification, crystals of metal which had been deposited electrolytically were fused in a current of hydrogen on a support of the purest lime. The adherent lime was removed by etching, and finally

<sup>14</sup> *Proc. Am. Acad.*, 40, 428 (1904); *THIS JOURNAL*, 26, 1587 (1904); *Z. anorg. Chem.*, 43, 25 (1905).

<sup>15</sup> *Proc. Am. Acad.*, 41, 77 (1905); *THIS JOURNAL*, 27, 879 (1905); *Z. anorg. Chem.*, 46, 40 (1905).

<sup>16</sup> *Ref. 13*, p. 1597; *Z. anorg. Chem.*, 70, 41 (1910).

<sup>17</sup> Baxter, Moore and Boylston, *THIS JOURNAL*, 34, 260 (1912).

<sup>18</sup> Baxter and Grover, *ibid.*, 37, 1030 (1915).

<sup>19</sup> Baxter, *ibid.*, 28, 1329 (1906). Sample E.

the buttons were washed, dried and heated in a vacuum at about 400°. (Sample I).

Another specimen, prepared by Richards and Hall,<sup>20</sup> had been finally precipitated as metal by ammonium formate, and the product was fused, etched and dried as stated above (Sample II).

As all the material had been standing for some years in desiccators, most of it was again slightly etched with nitric acid, dried and again heated in a vacuum, although this last process was omitted in Expts. 2 and 3.

### Description of Apparatus

The apparatus resembled very closely that used by Guye and Germann for the determination of small amounts of gases except that when first constructed no provision was made for analysis of the gas, and later, because the quantity of gas was found to be very small, it was not considered necessary to make the analysis. We have found the apparatus very satisfactory for the purpose.

The transparent quartz tube *AB*, in which the reactions were carried out was connected by a carefully ground joint *C* to the all-glass measuring apparatus. The tube *F* contained copper amalgam to prevent iodine vapor from reaching the mercury in *H* and *J*. Measurements of pressure were made in the McLeod gage *H*, which magnified the pressure 50 times. In order to dry the gas, *L* was filled with phosphorus pentoxide which had been freshly sublimed in a current of pure dry oxygen. A spectroscopic examination of the gas was made possible by the Plücker tube *R*, which was partially protected from mercury vapor by gold leaf in the tube *S*. The whole system could be exhausted by an automatic Töpler pump of the Maass<sup>21</sup> type. By means of the leveling bulb *W* the gas content of the apparatus could be largely transferred to *L* or back again to *AB*. Ground joints and stopcocks were made tight with Ramsay grease, especial pains being taken in the ground joint *C* to prevent contact of the grease with gases in the tube.

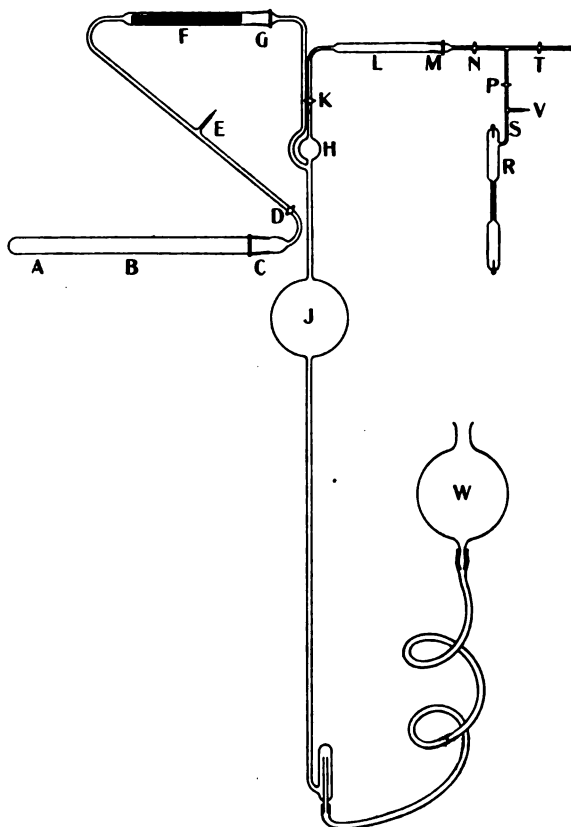
The method of procedure was in general as follows. The whole apparatus was exhausted through *T* and the stopcock *K* was closed. By raising the leveling bulb *W* the mercury was introduced into the gage *H* and the reading of the gage was taken. Then the stopcock *D* was closed and the reaction was carried out in *AB*. When the reaction was complete and the tube *AB* was cold, the stopcock *D* was opened and after the pressure had been given time to adjust itself, the reading of the gage *H* was taken. If it was desired to dry the gas, it was forced into *L* by filling *J* with *D* open, then closing *D* and by raising *X*, forcing all the gas through *K* into the drying tube. After closing *K* the process was repeated four times. When the gas was dry it was allowed to diffuse back again into *AB* and the pressure was remeasured. Although this method of determining the proportion of water vapor is obviously not highly exact, in view of the small quantities of gas ultimately found, the process is

<sup>20</sup> Richards and Hall, *THIS JOURNAL*, 39, 531 (1917).

<sup>21</sup> Maass, *ibid.*, 37, 2654 (1915).

amply accurate for the purpose. In a similar fashion the gas could be collected in *L* and then admitted to the Plücker tube *R*.

The quantity of gas was estimated from the difference between the gage readings before and after the experiment, and the volume of the system as far as the gage, and is expressed in terms of weight of gas per gram of material on the assumption that the density of the gas is as large as that of air. Since a portion of the gas was certainly water vapor and a portion of it was undoubtedly hydrogen, and as the other gases likely to be present,—carbon dioxide, carbon monoxide, oxygen and nitrogen,—with the exception of carbon dioxide possess nearly the same density as air, the above assumption seems to be a safe one.



### The Determination of Gases in Iodine

Since the determination of the gases in silver involved the reaction of silver with iodine, the first step in the problem was the determination of the gases in iodine. This was carried out by placing the iodine at *A* and then, after exhausting the tube, subliming the iodine from *A* to *B*



by warming the tube very gently at *A* and cooling it at *B* by means of a cloth wet with alcohol and with the assistance of a blast of air.

Most of the iodine could then be sublimed back to the point *A*, if desired, and the whole process could be repeated. Some iodine unavoidably reached the joint *C*, and even as far as the stopcock *D*, but the greater part remained in the quartz tube.

Because of the desirability of duplicating so far as possible the conditions used in preparing iodine for weighing for atomic weight work in the Harvard laboratory, and because in this work the iodine was always weighed after fusion in the weighing tube, the iodine was usually melted into the quartz tube and allowed to solidify in a fairly thin layer over the closed end of the tube. Thus, most of the material formed a compact mass, although of course a small proportion evaporated and condensed as crystals. In some cases a small amount of air apparently was trapped between the iodine and the glass, for the tube, after the preliminary exhaustion, showed a slight gain in pressure on standing. When this occurred the apparatus was allowed to stand exhausted until the pressure had become constant and remained so for some hours before the iodine was sublimed. In order to find out whether the surface exposed by the iodine plays an important part in the gas retention, in Expts. 3 and 6 the iodine was wholly in the form of loose crystals. The weight of iodine used in each experiment was found from the gain in weight of the reaction tube.

After Expt. 4 had been completed, a test was made to determine whether the quartz sublimation tube was perfectly tight. The empty quartz tube was exhausted and after the pressure had been read, the tube was heated as in an experiment with iodine. No change in pressure resulted. On further heating to a much higher temperature (about 500°), however, the interior pressure increased 0.054 mm. Since this increase might have been due to gases dislodged from the interior surface of the tube at the higher temperature, it was again exhausted and heated. The increase in pressure, 0.016 mm., though smaller, was disquieting. Therefore the whole tube was fire polished with an oxy-gas flame. Upon exhausting and heating to about 500° the pressure rose 0.014 mm., and after two days had increased only 0.010 in addition. Two later experiments of the same sort yielded still smaller gains, of 0.004 mm. in each case. Although it seems likely, therefore, that a small part of the increase in pressure in the experiments with iodine is not to be attributed to the iodine, this uncertainty is too small to be of importance in the final outcome.

In several experiments the iodine was subjected to repeated sublimation as described above (this page). The results of these experiments are collected in Table I. In accordance with the observations of Guye and Germann,<sup>22</sup> these results indicate clearly that gas evolution is essentially over in most

<sup>22</sup> *Compt. rend.*, 159, 226 (1914).

cases after one sublimation in vacuum and that two sublimations are invariably sufficient. Consequently in many of the later experiments only one sublimation was carried out.

TABLE I  
EFFECT OF REPEATED SUBLIMATION  
Increase in pressure in mm.  
Sublimation

Expt.	I	II	III	IV
2	0.146	0.020		
3	0.054	0.024	0.020	
4	0.154	0.106	0.000	0.004
5	0.446	0.020		
6	0.152	0.000		
8	0.144	0.020		
12	0.068	0.086		
14	0.070	0.006		

In Table II are given the results of all the experiments. In Expts. 1 to 9 the vacuum apparatus contained only iodine, in the remainder the examination of iodine was combined with that of silver, the iodine being first sublimed to free it from gases and then allowed to react with silver in a separate part of the experiment.

The following experiments indicate conclusively that the proportion of gas obtained is very largely dependent upon the purity of the iodine. In Expts. 13 to 18 not only was the material from which the iodine was prepared more carefully purified than for the previous experiments but the iodine was also passed over hot platinum gauze to ensure complete combustion and elimination of carbon compounds. Although these last six experiments yielded less than half as much gas as the general average of all the experiments and less than  $\frac{1}{3}$  as much as the crude iodine, even the crude material yielded considerably less than half as much gas as Guye and Germann obtained,<sup>23</sup> while our purest iodine, which was essentially identical with that used by Baxter in his last determination of the ratio of silver to iodine except that it had been subjected to a larger number of sublimations, was found to yield only 0.00015% of gas, slightly more than  $\frac{1}{10}$  that found by Guye and Germann. This proportion is far smaller than the experimental error of the process in which iodine was compared with silver.

Spectroscopic examination of the gases obtained in Expts. 3 and 9 showed the presence of hydrogen and carbon monoxide (besides mercury). The hydrogen spectrum may have had its origin in water held either by the iodine or the interior surfaces of the apparatus, and incompletely removed from the gas. The carbon spectrum undoubtedly is due largely

<sup>23</sup> Guichard in a similar experiment found 0.45 cc. of gas, per 100 g. of iodine. The percentage calculated as air is 0.0005, a proportion identical with ours obtained with crude iodine. *Compt. rend.*, 153, 272 (1911).

TABLE II  
GASES IN IODINE  
Volume of Apparatus = 180 cc.

Expt.	Sample of iodine	Wt. of iodine G.	Initial reading of gage Mm.	Final reading of gage Mm.	Change in pressure Mm.	Water vapor in gas %	Wt. of gas Mg.	Gas %
1	B	2.0	0.5	2.0	0.030		0.0096	0.00044
2	B	10.2	0.2	7.5	0.146		0.0418	0.00041
			1.7	2.7	0.020		0.0057	0.00006
3	A	5.6	0.3	3.0	0.054	7	Total	0.00047
			3.0	4.2	0.024		0.0154	0.00027
			4.2	5.2	0.020		0.0069	0.00012
							0.0057	0.00010
4	B	17.6	0.3	8.0	0.154	55	Total	0.00049
			8.0	13.3	0.106		0.0441	0.00025
			13.3	13.2			0.0303	0.00017
			13.2	13.5	0.004			0.00001
5	A	25.1	0.7	23.0	0.446	36	Total	0.00043
			23.0	24.0	0.020		0.1275	0.00051
							0.0057	0.00002
6	B	8.7	1.2	8.8	0.152		Total	0.00053
			8.8	8.8	0.000		0.0435	0.00050
7	C	5.7	2.1	7.0	0.098			0.0280
8	C	13.7	0.8	8.0	0.144			0.0412
			8.0	9.0	0.020			0.0057
9	C	5.8	0.8	4.4	0.072	6	Total	0.00034
10	C	11.8	1.0	8.3	0.146	39		0.0206
11	C	17.1	2.5	22.0	0.390			0.0417
12	D	14.0	0.5	3.9	0.068			0.1115
			3.9	8.2	0.086			0.0194
								0.0246
							Total	0.00032
13	D	5.9	0.8	1.9	0.022			0.0063
14	D	16.5	1.2	4.7	0.070			0.0200
			1.0	1.3	0.006			0.0017
15	D	12.1	1.2	8.0	0.136		Total	0.00013
16	D	15.9	1.0	4.6	0.072			0.0389
17	C	16.0	0.8	3.2	0.048			0.0206
18	Residues	13.6	0.5	3.1	0.052			0.0137
								0.0149
							Av.	0.00035
							Av. of Expts. 13 to 18	0.00015
							Av. of Expts. with Sample A	0.00051
							Sample B	0.00046
							Sample C	0.00038
							Sample D	0.00020

to carbon compounds contained in the iodine, since the proportion of gas obtained was very markedly diminished by the step taken to burn such substances. It is possible that the grease employed on the ground joints was responsible for a part of the gas. However, since the percentage of gas obtained is certainly a maximum and is so small as to be negligible from the standpoint of present atomic weight accuracy, no further attempt was made to discover the exact nature and source of the gas.

### The Determination of Gases in Silver

In the conversion of silver into silver iodide, a weighed quantity of silver was placed at the point *B* in the quartz tube with an excess of iodine at the point *A*. After the system had been exhausted, the iodine was once sublimed and the increase in pressure which resulted was used as a measure of the quantity of gases evolved from the iodine as already described. The apparatus was then exhausted a second time and the portion of the tube where the silver was located was heated to a temperature somewhat above the melting point of silver iodide,  $530^{\circ}$ , so that the product of the reaction flowed away from the residual metal, leaving a fresh surface for attack. The reaction progressed rather slowly, several hours being necessary for even approximately complete conversion of the silver into iodide. In fact in many cases the experiment was stopped while a residue of unconverted silver still remained and, after the gas determination was completed, this residue was cleaned, weighed and the weight was subtracted from that originally taken. When the conversion of silver to iodide was over, the pressure in the apparatus was measured as previously described. In the first four experiments the proportion of water vapor in the gases also was measured.

After the first two experiments with silver had been completed, the suspicion arose that gas might result either by evolution from or diffusion through the quartz tube at the point of heating. Blank experiments in which the empty tube was exhausted and heated at one spot for several hours to the same temperature as in the experiment with silver, showed increases in pressure of 0.038 and 0.030 mm. Although these gains are small, the attempt was made to diminish the uncertainty by again fire polishing the greater part of the tube with an oxy-gas flame. Repetition of the blank experiments showed increases in pressure of 0.020 and 0.016 mm. and a short but intense heating of nearly the whole tube produced an increase in pressure of only 0.008 mm. Preparatory to all subsequent experiments with silver the section of the tube which had been heated in the previous experiment was fire polished. In spite of this precaution it seems likely at any rate that a small part of the observed increase in pressure in the experiments with silver had its source in the tube itself.

While there seems to be evidence that at elevated temperatures quartz

is pervious to gases, especially hydrogen,<sup>24</sup> we are of the opinion that with our tube a part of the difficulty originally was due to minute striations which were closed by the fire polishing.

Of course, unavoidably the silver buttons were very superficially attacked at ordinary temperature by the iodine during the exhausting of the tube and the determination of the gases in the iodine. The greater part of any gas thus produced must have been included in that evolved during the sublimation of the iodine.

In Expts. 6 to 10 the gas evolved during the early stages of the conversion of the silver to iodide at high temperature was measured. Then the tube was again exhausted and the reaction completed. On an average this gas obtained from the surface of the silver amounts to about one third of the whole. Although the quantities involved are too small to be viewed as positive proof, this result seems to be some indication that the surface of the silver contains a larger proportion of gases than the interior, a conclusion diametrically opposite to that arrived at by Guye and Germann.<sup>25</sup>

The following table (III) gives the results of all the experiments with silver. In Expts. 6 to 10 the first series of figures in each experiment refers to the gas evolved from the surface of the silver, the second series refers to that subsequently obtained.

It is interesting to note that in Expt. 1 with crude (99.86%), large silver wire, the proportion of gas obtained is slightly greater than that obtained by Guye and Germann from their purer material (0.0042%), but is considerably less than they found in their crude metal (0.024%). So far as the results show there is no difference between silver precipitated electrolytically before fusion (Sample I) and that precipitated with formate (Sample II). On the whole the average of Expts. 4 to 10 seems to give the most reliable estimate of the gas content of the silver, since the material used in Expts. 2 to 3 had been exposed to the atmosphere of desiccators sealed with grease for some years and was not given preliminary cleansing. Furthermore, in Expts. 1 and 2 evidence was secured that slight leakage through the quartz tube had occurred.

As in the case of iodine the final result represents a maximum, both because of the possibility of the evolution of gases from the interior of the apparatus and that of leakage through the quartz tube. The result, 0.00063%, even if real, is almost negligible at the present stage of atomic weight accuracy.

Spectroscopic examination of the gases obtained in Expt. 2 indicated the presence of both hydrogen and carbon monoxide. The gas obtained

<sup>24</sup> Villard, *Compt. rend.*, 130, 1752 (1900). Jacquerod and Perrot, *Arch. sci. phys. chem.*, 18, 613 (1904); 20, 454 (1905). Richardson and Richardson, *Phil. Mag.*, 22, 704 (1911). Mayer, *Phys. Rev.*, 6, 288 (1915).

<sup>25</sup> Ref. 7, p. 228.

in Expt. 3, however, gave only the hydrogen spectrum. This evidence is interesting since it indicates that the gas obtained from silver is at any rate largely composed of this relatively light gas.

TABLE III  
GASES IN SILVER  
Volume of Apparatus = 180 cc.

Expt.	Sample of silver	Wt. of silver G.	Initial reading of gage Mm.	Final reading of gage Mm.	Change in pressure Mm.	Water vapor in gas %	Wt. of gas Mg.	Gas %
1	Crude	5.2	0.8	56.6	1.132	13	0.324	0.00623
2	I	3.6	0.7	10.0	0.186	30	0.0532	0.00148
3	I	5.2	0.7	17.2	0.330	13	0.0858	0.00182
4	I	4.6	0.7	4.3	0.072	33	0.0206	0.00045
5	I	3.8	1.8	8.2	0.128		0.0366	0.00096
6	I	7.1	1.2	5.0	0.076		0.0218	0.00031
			1.3	7.0	0.114		0.0326	0.00046
Total								0.00077
7	I	5.6	2.0	3.8	0.036		0.0103	0.00018
			1.0	5.1	0.082		0.0234	0.00042
Total								0.00060
8	II	6.0	1.2	2.8	0.032		0.0091	0.00015
			1.0	3.5	0.050		0.0143	0.00024
Total								0.00039
9	I	5.7	5.0	6.8	0.036		0.0103	0.00018
			1.0	5.0	0.080		0.0329	0.00040
Total								0.00058
10	II	3.4	1.3	2.2	0.018		0.0052	0.00015
			0.5	3.4	0.058		0.0166	0.00049
Total								0.00064
Av., excluding Expt. 1								0.00085
Av., excluding Expts. 1 to 3								0.00063
Av. of Expts. 4, 5, 6, 7 and 9								0.00067
Av. of Expts. 8 and 10								0.00052

Since the hydrogen is liberated from the silver in the presence of an excess of iodine, and therefore may have combined in part with the iodine, the question may very well be raised as to whether all the hydrogen originally contained by the silver is eventually recovered. Aside from the possibility of adsorption on the interior surfaces of the system, any hydrogen iodide produced would have exerted twice the pressure of the hydrogen it replaced. It seems reasonable to assume at any rate that one effect compensated the other.

If the gas obtained from the silver is largely hydrogen, as seems likely, from the spectroscopic results, the percentage is 0.00004. Since, however,

a considerable proportion of the gas was found to be water vapor, the real proportion must be somewhat larger than this. For instance, if  $\frac{1}{3}$  is water vapor, the percentage of gas is 0.00016.

This proportion of hydrogen is smaller than that obtained by others in the past in silver which had been heated in hydrogen. Graham<sup>26</sup> found on an average 0.0005%. Stas<sup>27</sup> concluded the proportion to be less than 0.0004%. Mallet's<sup>28</sup> result was 0.0003%, and Baxter's<sup>29</sup> 0.001%, while Richards and Wells<sup>30</sup> found that silver which had been fused in hydrogen produced exactly as much silver chloride as metal which had been fused in a vacuum, within less than 0.001%.

The effect of impurities in iodine and silver upon the results of experiments in which they play a part depends upon the directness with which the calculations may be computed. One of the least favorable cases, used as an example by Guye,<sup>31</sup> is that of the ratios  $I_2O_5:2Ag$ , and  $I_2:2Ag$ , from which the atomic weights of silver and iodine may be computed. Impurity in the iodine alone produces a positive error in the atomic weight of silver. Impurity in the silver alone also produces a positive error. Impurities in both silver and iodine produce an effect depending upon the relative proportions.

In the following table are given the values obtained by applying corrections of the magnitude observed by us, to the results of Baxter and Tilley,<sup>32</sup> and Baxter<sup>18</sup> on the above ratios.

	Uncorrected	Per cent. of gas Ag 0.00063 I 0.00046	Per cent. of gas Ag 0.00016 I 0.00015
At. wt. Ag.....	107.864	107.862	107.864
At. wt. I.....	126.913	126.912	126.913

Only upon the most unfavorable interpretation of the results in this paper are the atomic weights in question affected by as much as 0.002 unit.

### Summary

1. Iodine sublimed in air was found to yield small quantities of gas when resublimed in a vacuum. The proportions varied from 0.0005% in the case of crude iodine, to 0.00015% in the case of the purest material. These proportions are far smaller than those found by Guye and Germann.

2. Crude silver, when converted to iodide in a vacuum, was found to yield 0.006% of gas, while the purest material when treated in the same

<sup>26</sup> Graham, *Phil. Mag.*, **32**, 503 (1866).

<sup>27</sup> Stas, "Oeuvres Complètes."

<sup>28</sup> Mallet, *Phil. Trans.*, **171**, 1020 (1880).

<sup>29</sup> Baxter, *Am. Chem. J.*, **22**, 362 (1899).

<sup>30</sup> Richards and Wells, *Carnegie Inst. Pub.*, **28**, 23 (1905).

<sup>31</sup> Ref. 7, p. 237.

<sup>32</sup> Baxter and Tilley, *THIS JOURNAL*, **31**, 201 (1909).

way yielded  $1/10$  as much, 0.00063%. In this case also the proportion of gas found in pure metal is only  $1/7$  that found by Guye and Germann.

The foregoing figures are based on the assumption that the iodine and the silver are responsible for all the gas evolved and that the gas is as heavy as air.

The likelihood has been pointed out that a portion of the gas obtained either was liberated from the walls of the apparatus or diffused through the reaction tube. Furthermore in the case of silver at any rate a large portion of the gas was found to be hydrogen. Therefore there is good reason to believe that the real percentages are smaller than those given above.

3. Even when maximum corrections are applied, the atomic weights of silver and of elements referred to silver are affected in the most unfavorable cases by only 0.002 unit.

A grant from the Wolcott Gibbs Fund of the National Academy of Sciences has materially aided the prosecution of this investigation.

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## THE PURITY OF ATOMIC WEIGHT SILVER. II. SOLID IMPURITIES

BY GREGORY PAUL BAXTER

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The preparation of silver of the highest purity for purposes of atomic weight comparison has been the subject of many investigations, the most recent of which is that of Richards and Wells,<sup>1</sup> who found that the processes of precipitation as silver chloride, crystallization of silver nitrate, precipitation of the metal from solution by ammonium formate,<sup>2</sup> and electrolytic transport of the metal from a dissolving anode through a concentrated solution of silver nitrate,<sup>3</sup> are all effective in removing metallic impurities. In investigations in the Chemical Laboratories of Harvard University various combinations of these methods have been used both before and since the investigation of Richards and Wells, and the products have been found to yield identical results within the experimental error.<sup>4</sup>

The final treatment of the silver before weighing has consisted almost

<sup>1</sup> Richards and Wells, *Carnegie Inst. Pub.*, 28, 16 (1905); *THIS JOURNAL*, 27, 459 (1905).

<sup>2</sup> Stas, "Oeuvres Complètes," vol. 3, p. 40.

<sup>3</sup> Abrahall, *J. Chem. Soc.*, 61, 660 (1892).

<sup>4</sup> Guye has recently questioned the freedom of such material from metallic impurities. *J. chim. phys.*, 15, 554 (1917).



invariably of fusion on a boat of carefully purified lime, usually in a current of hydrogen,<sup>5</sup> but sometimes in a vacuum. If the silver has been deposited from a silver nitrate solution, fusion in a vacuum was found by Richards and Wells to be insufficient, for the residual metal seems to retain a small amount of oxygen coming from the included pockets of silver nitrate solution.<sup>6</sup> If electrolytic crystals are fused in hydrogen, however, the latter difficulty disappears, and this process, namely, fusion of the metal in a current of hydrogen on a boat of pure lime, has been utilized exclusively in recent years. When thus fused, the buttons, although bright, are coated with specks of adherent lime which must be removed by etching with dil. nitric acid several times. In this way a layer of silver of considerable thickness is removed. The final product, after being washed and dried is then heated to about 500° in a vacuum.

Naturally the possibility exists of the presence of calcium and occluded hydrogen in the silver. The first point was considered very carefully by Richards and Wells who were unable to detect calcium by a wet process in a 10g. sample of silver which had been fused upon lime.<sup>7</sup> Their experiment showed that the metal certainly contained less than 0.0001% of calcium.

Furthermore, Stas concluded that silver which had been fused and cooled in hydrogen does not contain more than 0.0004% of this element, and the experiments recorded in the preceding paper prove that the total gaseous impurity in the silver in question is *less than* 0.0006%.<sup>8</sup> This quantity is barely significant in work of the utmost accuracy at the present time.

Since the spectroscope is a most uncompromising and sensitive instrument for the detection of metallic impurities and because of the success which has attended spectroscopic examination of pure metals for exact purposes in this Laboratory in recent years,<sup>9</sup> a careful spectroscopic examination of several specimens of very pure silver has been carried out. To do this both the spark and the arc spectra between electrodes of the purest silver have been photographed and compared with spectra of various possible impurities produced under exactly similar conditions. Several different samples of silver which have been used in recent atomic weight comparisons have been examined.

One group of specimens had been subjected to essentially the same processes.

<sup>5</sup> Baxter, *Proc. Am. Acad.*, 39, 249 (1903).

<sup>6</sup> Ref. 1, p. 23.

<sup>7</sup> Ref. 1, p. 22.

<sup>8</sup> See also: Graham, *Jahresb.*, 1866, 51. Neumannn and Streintz, *Monatsh.*, 12, 642 (1891). Baxter, *Am. Chem. J.*, 22, 362 (1899).

<sup>9</sup> Baxter and Hartmann, *THIS JOURNAL*, 37, 116 (1915). Baxter and Grover, *ibid.*, 37, 1032, 1050 (1915). Baxter and Grose, *ibid.*, 38, 859, 869 (1916).

The first step consisted of double precipitation of silver chloride, with either intermediate reduction by means of sugar and sodium hydroxide, and solution of the metal in nitric acid, or solution of the first precipitate of silver chloride in ammonia and reprecipitation with nitric acid. After the chloride had been reduced with sugar and the metal fused on charcoal, the buttons were cleansed and dissolved in nitric acid, and the solution was heated with an excess of ammonium formate. The washed precipitated silver was again fused in air on a porcelain crucible lined with the purest lime, and then the buttons were made the anode under a concentrated solution of silver nitrate made from one of the buttons. The electrolytic crystals were fused in a current of the purest hydrogen on a boat of pure lime, contained in a porcelain tube. Finally the buttons were several times etched with small portions of dil. nitric acid, and after thorough washing and drying in the air were heated in a hard glass or quartz tube to about 500°. Four different specimens of this variety of silver were examined. One had already been used by Baxter, Moore and Boylston,<sup>10</sup> and three others had been prepared for work at present under way by Messrs. O. J. Stewart and Muneo Tani and Dr. P. F. Weatherill.

In the other group of specimens, crystallization of silver nitrate from dil. nitric acid was followed by precipitation of the metal with ammonium formate, and the product was fused in hydrogen on lime as described above. One of these specimens had been used by Richards and Wells<sup>1</sup> and had been crystallized 15 times as silver nitrate before precipitation with ammonium formate. The other had been used by Richards and Willard<sup>11</sup> and had been crystallized 5 times as silver nitrate before the formate precipitation. It is to be noted that one of the chief differences between the two groups is that in the former case, the material before the final fusion consisted of fairly large electrolytic crystals, in the latter case of finely divided precipitated metal.

The spectrograms were taken with a Féry quartz spectrograph, which by means of a diaphragm permits the close juxtaposition of successive spectra without involving any movement and therefore lateral displacement of the film holder. The spark was produced by means of a half kilowatt wireless transformer, actuated by the 110 volt a. c. lighting current, with a condenser parallel with the spark and with sufficient self inductance in series with the spark to eliminate the air lines almost completely. In character the spectrum fell midway between an arc spectrum and that produced with the usual high tension interrupting coil. The arc was produced by stepping down with resistance a 110 volt d. c. current so that approximately 15 amperes passed between the points. The electrodes, which weighed 5 or more grams each, were held between the points of clean steel pincers in such a way that the arc or spark did not approach the steel.

The silver was compared with the following metals: magnesium, zinc, cadmium, mercury, aluminum, chromium, iron, nickel, copper, gold, platinum, tin, lead, calcium and bismuth. This list includes all the metals found in commercial silver by de Gramont.<sup>12</sup>

Although the exposures were prolonged, two minutes or more in every

<sup>10</sup> Baxter, Moore and Boylston, *THIS JOURNAL*, **34**, 280 (1912).

<sup>11</sup> Richards and Willard, *Carnegie Inst. Pub.*, **125**, 16 (1910); *THIS JOURNAL*, **32**, 18 (1910).

<sup>12</sup> de Gramont, *J. chim. phys.*, **14**, 336 (1916).

case, not the smallest trace of any one of these metals could be discovered, with the sole exception of calcium. Calcium lines were faintly visible in every one of the specimens with slightly varying intensity. Comparison of the spectrograms with others of metals containing known proportions of impurity indicates that the proportion of calcium in even the least pure specimen is of the order of one part in a million. This is in entire accord with the experiment of Richards and Wells mentioned above. Furthermore, in the specimen prepared by Richards and Willard the two strongest lines of silicon are very faintly visible. Here again the proportion seems to be extremely small, not greater than, if as great as, the proportion of calcium.

Nevertheless, a further attempt was made to discover the proportion of calcium as follows.

All the buttons which had been used in the spectroscopic experiments, 78 g. in all, were once more slightly etched with dil. nitric acid in order to remove surface impurities acquired during handling. This could hardly have altered the composition of the silver since all the material had previously been etched several times in the same way. The material was then dissolved in a platinum dish in nitric acid which had been distilled through a quartz condenser, and about half of the silver was next deposited electrolytically chiefly upon the dish which was made the negative pole, but partly as peroxide on the anode. The electrolyte was evaporated nearly to dryness in another platinum dish over an electric stove, and after solution of the residue in the purest water about half the remaining silver was deposited electrolytically.

Evaporation and a third electrolysis removed all but traces of the silver. The final electrolyte was evaporated to dryness and the solution of the residue in water was saturated with hydrogen sulfide to remove the last traces of silver. After filtration, a slight excess of ammonia, in the form of gas, was introduced to remove a trace of iron which originated in the steel pincers used for holding the buttons during the spectroscopic experiments. The volume of the solution at this stage was about 20 cc. Filtration and evaporation to dryness in a weighed platinum crucible followed, and the residue was heated to about 600° to expel ammonium salts. The residue weighed 0.12 mg. When dissolved in a few drops of very dilute nitric acid and made alkaline with ammonia the solution gave a barely visible precipitate with ammonium oxalate in a volume of about 1 cc., while 0.03 mg. of calcium under similar conditions gave a distinctly heavier precipitate.

The proportion of calcium in the silver therefore did not exceed 0.00004 % on an average, somewhat less than the estimate made above, and in entire accord with the experiments of Richards and Wells.

### Summary

It is evident therefore that in the present state of the most accurate chemical analysis the purity of these specimens of silver is considerably more than sufficient.

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[CONTRIBUTION FROM THE T. JEFFERSON COOLIDGE, JR., CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

## THE SIGNIFICANCE OF THE DENSITY OF HYDROGEN BROMIDE WITH REFERENCE TO THE ATOMIC WEIGHT OF BROMINE

BY GREGORY PAUL BAXTER

Received December 23, 1921

The numerous researches upon the densities of various gases, carried out under the direction of P. A. Guye at the University of Geneva have furnished very interesting information as to the molecular weights of the substances examined, and either directly or indirectly as to the atomic weights of the various elements involved. These experiments have been executed with exceptional care and skill, and represent a great advance in the technique of both the preparation of pure gases and the experimental determination of gas densities.

The values found for the atomic weights in most cases corroborate in such a reassuring way the results of older methods involving gravimetric ratios between solid, and sometimes liquid, substances, that the Swiss investigators have been led to assign a significance to the gas density results which possibly is in excess of their real value. Recently, for instance, Guye<sup>1</sup> has applied the results of experiments upon the density of hydrogen bromide to the determination of the atomic weight of bromine and, partly on this basis, partly on other grounds, insists upon a correction for the atomic weight of silver. Questions concerning the atomic weight of silver have already been dwelt upon in some detail in two preceding papers.<sup>2</sup> The purpose of the present paper is to call attention to some uncertainties involved in the gas density method of determining molecular weights, as applied in the case under consideration.

In the discussion referred to above, Guye computes the molecular weight of hydrogen bromide by a modification of Berthelot's "limiting density" method. In the expression used

$$M = 32 \frac{d_{\text{HBr}}}{d_{\text{O}_2}} \times \frac{(1 + \lambda)_{\text{O}_2}}{(1 + \lambda)_{\text{HBr}}}$$

$d$  represents the weight of the normal liter and  $1 + \lambda$  is equal to  $\frac{P_0 V_0}{P_1 V_1}$ ,

the ratio of the values of  $PV$  at zero pressure and 1 atmosphere respectively. The value of  $M$  thus depends directly upon four experimentally determined quantities, namely, the two densities and the two values of  $1 + \lambda$ . The last two values obviously cannot be measured directly, but must be found by extrapolation from values determined at pressures between zero and one atmosphere. It is clear that where the value of

<sup>1</sup> Guye, *J. chim. phys.*, 17, 171 (1919).

<sup>2</sup> Baxter, *THIS JOURNAL*, 44, 577, 591 (1922).

$1 + \lambda$  is not far from unity, as in the case of oxygen, the extrapolation can be done with far greater certainty than with a gas like hydrogen bromide where  $1 + \lambda$  is very nearly 1.01.

Of the two densities, that of oxygen is unquestionably known with the greater accuracy, for the uncertainty is no greater than a few parts in one hundred thousand. Lord Rayleigh's value for the weight of the normal liter, 1.42904 g., has been used by Guye in the foregoing formula. The value of  $1 + \lambda$  for oxygen used by Guye, 1.00097, probably represents an accuracy nearly if not quite as great as that of the density of oxygen.

The chief uncertainties fall, therefore, upon the data referring to hydrogen bromide. As regards the density of the gas, three determinations of the density of hydrogen bromide have been carried out at the University of Geneva, by Moles,<sup>3</sup> by Reiman<sup>4</sup> and by Murray.<sup>5</sup> The gas was prepared by many different methods and the experiments were carried out in globes of different capacities. The divergences do not group themselves in any systematic manner, so that the results may be treated either as one single series or separately in the case of different experimenters, the method which has actually been followed by Guye. In the final discussion Guye rejects the experiments by Murray as being on the whole less reliable than the others.

In all, 33 determinations of the density were made by Moles at atmospheric pressure, varying from 3.64608, to 3.64298, an extreme difference of 0.00310, or 0.085%. The probable error of the mean is  $\pm 0.00008$ , or 0.002%. Reiman made 31 determinations varying from 3.64694 to 3.64199, with an extreme difference of 0.00495 or 0.134%. The probable error is  $\pm 0.00014$ , or 0.004%.

The averages of the two series, 3.64442 and 3.64419, are subsequently subjected to various small corrections<sup>6</sup> and become 3.64441 and 3.64404. It seems probable that the mean value, 3.64423, represents this constant with an accuracy of 0.01%, but in view of the rather disconcerting variation of the individual determinations and the commonly recognized principle that the probable error as calculated by the method of least squares is likely to lead to a false idea of accuracy in a series of less concordant experiments, it is questionable whether the real accuracy is greater than the above estimate.

The values of  $1 + \lambda$  for hydrogen bromide are found from the experimental values for  $PV$  at 1,  $\frac{2}{3}$  and  $\frac{1}{3}$  atmospheres. To do this the weight of a liter of gas at 0°, and at  $\frac{2}{3}$  and  $\frac{1}{3}$  atmospheres is first found by ex-

<sup>3</sup> Moles, *J. chim. phys.*, **14**, 389 (1916).

<sup>4</sup> Reiman, *ibid.*, **15**, 293 (1917).

<sup>5</sup> Murray, *ibid.*, **15**, 334 (1917).

<sup>6</sup> Ref. 1, pp. 174, 181.

periment. The ratios of  $\frac{2}{3}$  and  $\frac{1}{3}$  the weight of a liter at 1 atmosphere to the weights of one liter at  $\frac{2}{3}$  and  $\frac{1}{3}$  atmospheres give the values of  $PV$  referred to the product at 1 atmosphere taken as unity.

Moles's corrected value for the density at  $0^\circ$  and  $\frac{2}{3}$  atmosphere is  $2.42203 \pm 0.00019$  with an extreme difference of 0.00297 or 0.12%, while Reiman's result is  $2.42190 \pm 0.00023$  with an extreme difference of 0.00606 or 0.25%.

At  $\frac{1}{3}$  atmosphere Moles's figure is  $1.20737 \pm 0.00015$  with an extreme difference of 0.00254 or 0.21% and Reiman's is  $1.20721 \pm 0.00009$  with an extreme difference of 0.00241 or 0.20%.

Since even the "probable errors" of the means at  $\frac{2}{3}$  atmosphere are 0.008% and 0.010%, while those at  $\frac{1}{3}$  atmosphere are 0.012% and 0.008%, it seems very doubtful whether the values of the densities at  $\frac{2}{3}$  and  $\frac{1}{3}$  atmospheres, and therefore the values of  $PV$  which are directly proportional to them, are known with an accuracy of  $\frac{1}{10000}$ .

Furthermore, it is noticeable that the values obtained by Reiman are consistently lower than those obtained by Moles by about 0.01%. The two series of results are summarized in the following table.

$P$ Atmospheres	Moles	Reiman	Difference	Percentage difference
1	$3.64441 \pm 0.00008$	$3.64404 \pm 0.00014$	-0.00038	-0.010
$\frac{2}{3}$	$2.42203 \pm 0.00019$	$2.42190 \pm 0.00023$	-0.00013	-0.005
$\frac{1}{3}$	$1.20737 \pm 0.00015$	$1.20721 \pm 0.00009$	-0.00016	-0.013

From these figures the values of  $PV$  at different pressures referred to that at one atmosphere as unity can be computed by the method outlined on pp. 596-7. The figures in parentheses are calculated from the densities found by Moles. The others are those used by Guye.<sup>7,8</sup>

$P$ Atmospheres	Moles $PV$	Reiman $PV$
1	1.000000	1.000000
$\frac{2}{3}$	(1.003127)	
	1.003105	1.003077
$\frac{1}{3}$	(1.006157)	
	1.006218	1.006190

Extrapolation of these figures for zero pressure was done by various methods, of which the two upon which most reliance is placed will be discussed. One of these is the "method of secondary differences,"<sup>9</sup> which is

<sup>7</sup> Ref. 1, p. 181.

<sup>8</sup> This discrepancy appears in Moles's paper, (Ref. 3, p. 431) and also in Guye's (*J. chim. phys.*, 17, 181 (1919)). In both places the weight of one liter of gas at 760 mm. seems to have been incorrectly calculated from the weights at  $\frac{2}{3}$  and  $\frac{1}{3}$  atmosphere.

<sup>9</sup> A simpler method of applying this method is as follows:  $(PV)_0 = (PV)_{\frac{1}{4}} + ((PV)_{\frac{1}{4}} - (PV)_{\frac{3}{4}}) + ((PV)_{\frac{1}{4}} - (PV)_{\frac{3}{4}}) - ((PV)_{\frac{3}{4}} - (PV)_1) = (PV)_1 - 3(PV)_{\frac{3}{4}} + 3(PV)_{\frac{1}{4}}$ .

illustrated by the following examples. The figures in parentheses represent extrapolated values.

Moles (Uncorr.)			
$P$ Atmospheres	$PV$	$\Delta_1 \times 10^6$	$\Delta_2 \times 10^6$
1	1.000000		
		3105	
$\frac{2}{3}$	1.003105		8
		3113	
$\frac{1}{3}$	1.006218		(8)
		(3121)	
0	(1.009339)		
Moles (Corr.)			
1	1.000000		
		3127	
$\frac{2}{3}$	1.003127		97
		3030	
$\frac{1}{3}$	1.006157		(97)
		(2933)	
0	(1.009090)		
Reiman			
1	1.000000		
		3077	
$\frac{2}{3}$	1.003077		36
		3113	
$\frac{1}{3}$	1.006190		(36)
		(3149)	
0	(1.009339)		

It is noticeable that while Moles's uncorrected results give a value for  $(PV)_0$  which is identical with that of Reiman in spite of the divergence of the individual density values, when Moles's results are corrected for apparent errors in calculation the divergence is pronounced, amounting to 0.025%. This affects the atomic weight of bromine by 0.02 unit.

Since the values of  $PV$  are inversely proportional to the density at any pressure, an error of 0.01% in any one value of the density has a marked influence upon the extrapolated value of  $(PV)_0$ . For instance in the following two tables the values of  $PV$  at  $\frac{2}{3}$  and  $\frac{1}{3}$  atmospheres are respectively increased by 0.01% over the experimental values found by Reiman.

$P$ Atmospheres	$PV$	$\Delta_1 \times 10^6$	$\Delta_2 \times 10^6$
1	1.000000		
		3177	
$\frac{2}{3}$	1.003177		164
		3013	
$\frac{1}{3}$	1.006190		(164)
		(2849)	
0	(1.009039)		

1	1.000000	3077	
$2/3$	1.003077	3213	136
$1/3$	1.006290	(3349)	(136)
0	(1.009639)		

In both cases the percentage effect upon the extrapolated value of  $(PV)_0$  is *three times as large* as the assumed difference, but in *opposite directions*. Thus an experimental error of 0.01% in the density at either  $2/3$  or  $1/3$  atmosphere affects the molecular weight of hydrogen bromide and the atomic weight of bromine by 0.03% or 0.024 unit. Such an error is admittedly within the experimental error of the density determinations. Because of this greater sensitiveness to experimental error at the lower pressures, it is unfortunate that less attention seems to have been given to the determinations under these conditions.

A second method of extrapolation upon which reliance is placed is the "algebraic method," with the use of equations of the following type

$$PV = 1 + \alpha - aP - bP^2$$

although in reality there is no difference between this method and the former one.

Obviously the last two terms disappear when  $P = 0$ . Then  $(PV)_0 = 1 + \alpha = 1 + \lambda$ . The term  $\alpha$  is found by solution of three equations involving three values of  $PV$ .  $PV$  and  $P$  at one atmosphere are both assumed to be unity.

$$\alpha = \left( (PV)_1 - 1 \right) \frac{P_2}{(1 - P_2)(P_1 - P_2)} - \left( (PV)_2 - 1 \right) \frac{P_1}{(1 - P_1)(P_2 - P_1)}$$

If  $P_1$  and  $P_2$  are taken as  $2/3$  and  $1/3$ , respectively, the expression simplifies to the form

$$\alpha = -3(PV)^{2/3} + 3(PV)^{1/3}$$

and

$$(PV)_0 = 1 - 3(PV)^{2/3} + 3(PV)^{1/3}.$$

Mathematically this method is identical with the "method of secondary differences" (see p. 597) and of course gives results identical with those of the latter method and equally sensitive to errors in the experimental values of  $PV$  from which the value of  $\alpha$  is computed; that is, a given percentage error in the experimental value of  $PV$  at  $2/3$  or  $1/3$  atmosphere is multiplied three times in the value of  $1 + \alpha$ , and hence in the molecular weight of hydrogen bromide.

Upon the assumption that each experimental value upon which the final value of the molecular weight of hydrogen bromide is dependent is in error by 0.01%, and upon the assumption that the effects of all errors are in the same direction, the sum total is 0.07%.



Pressure atmosphere	Density error %	Effect of error %
1	+0.01	+0.01
$\frac{2}{3}$	-0.01	+0.03
$\frac{1}{3}$	+0.01	+0.03
		<hr/>
Total		+0.07

In view of this unlikely but not impossible unfortunate combination of circumstances, the molecular weight of hydrogen bromide as found by this method is uncertain by 0.07% or 0.056 unit, and a similar uncertainty exists in the atomic weight of bromine.

While it is only fair to say that the above estimate of the error of the method is probably excessive, even if the total effect were only  $\frac{1}{3}$  as large, the uncertainty in the atomic weight of bromine would be 0.019 unit. It is unlikely that the present uncertainty in the value of the atomic weight of bromine referred to oxygen is as much as 0.01 unit, while the ratio of bromine to silver is apparently known with far greater accuracy.

From Moles's results Guye calculates the atomic weight of bromine to be 79.923, from Reiman's 79.915, from the average density, 79.920. The foregoing considerations indicate that the concordance of this result with that of the gravimetric ratio of bromine to silver<sup>10</sup> (79.916 if Ag = 107.88; 79.909, if Ag = 107.87) is in considerable measure fortuitous.

### Summary

The foregoing brief discussion illustrates some of the pitfalls which beset the gas density method of determining molecular weights. No method of extrapolation can be satisfactory or convincing where, as in this case, the accuracy of the numerical data diminishes as the region to be extrapolated is approached. The conclusion cannot be avoided that while in the case of hydrogen bromide the gas density method of determining molecular weights may be looked upon as an interesting and satisfactory corroboration of gravimetric evidence, its value ceases at that point. To use such evidence as a criterion upon which to judge the best gravimetric evidence, cannot be justified upon scientific grounds.

On the other hand, from the standpoint of the universal application of Avogadro's hypothesis to gases at low pressures, the results of the very careful density determinations in the laboratory of Professor Guye are particularly significant and convincing.

CAMBRIDGE 38, MASSACHUSETTS

<sup>10</sup> Baxter, *Proc. Am. Acad.*, 42, 201 (1906); *THIS JOURNAL*, 28, 1322 (1906); *Z. anorg. Chem.*, 50, 389 (1906).

[CONTRIBUTION FROM THE WOLCOTT GIBBS MEMORIAL LABORATORY OF HARVARD UNIVERSITY]

## THE ELECTROCHEMICAL BEHAVIOR OF LIQUID SODIUM AMALGAMS

BY THEODORE W. RICHARDS AND JAMES BRYANT CONANT

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The significance of the electrochemical behavior of amalgams in relation to the general behavior and nature of solutions as well as in relation to the laws of thermodynamics has already been often emphasized. The literature upon the subject is copious, and lack of space prevents a detailed review. Some of the more important papers are named in the accompanying list, in which the several Harvard investigations upon this subject during the last 23 years are placed at the conclusion.<sup>1</sup>

Sodium amalgam presents points of especial interest not only because the substance is so much used as a reducing agent, but also because the great affinities involved might lead one to expect extreme deviation from the simple concentration laws. Moreover, conflicting data concerning it have been published, without as yet having been reconciled.<sup>2</sup>

Accordingly the careful investigation of sodium amalgam was undertaken some years ago. The electrochemical part was finished early in 1916; the thermochemical part, which will soon be published, was studied with the help of Mr. John Russell in 1921.

<sup>1</sup> Tammann, *Z. physik. Chem.*, **3**, 441 (1889). Ramsay, *J. Chem. Soc.*, **55**, 521 (1889). Von Türin, *Z. physik. Chem.*, **5**, 340 (1890). Meyer, *Wied. Ann.*, **40**, 244 (1890). Meyer, *Z. physik. Chem.*, **7**, 477 (1891). Kerp, *Z. anorg. Chem.*, **17**, 284 (1898); **25**, 1 (1900). Cady, *J. Phys. Chem.*, **2**, 551 (1898); **3**, 107 (1899) (corr.). Schoeller, *Z. Elektrochem.*, **5**, 259 (1898). Maey, *Z. physik. Chem.*, **29**, 119 (1899). Kurnakov, *Z. anorg. Chem.*, **23**, 439 (1900). Haber, *Z. physik. Chem.*, **41**, 399 (1902). Haber and Sack, *Z. Elektrochem.*, **8**, 245 (1902). Schüller, *Z. anorg. Chem.*, **40**, 385 (1904). G. McP. Smith, *Am. Chem. J.*, **36**, 124 (1906); **37**, 506 (1907); **38**, 671 (1907). Von Wogau, *Ann. Physik.*, **23**, 345 (1907). Smith, *Z. anorg. Chem.*, **58**, 394 (1908). G. A. Hulett and DeLury, *THIS JOURNAL*, **30**, 1805 (1908). Smith and Bennett, *THIS JOURNAL*, **32**, 622 (1910). K. Bornemann and others, *Metallurgie*, **7**, 396 (1910); **9**, 473 (1912); Lewis and Kraus, *THIS JOURNAL*, **32**, 1459 (1910). Vanstone, *Chem. News*, **103**, 181 (1911); *J. Chem. Soc.*, **105**, 2617 (1914). Hildebrand and Eastman, *THIS JOURNAL*, **36**, 2020 (1914); **37**, 2452 (1915). MacInnes and Parker, *ibid.*, **37**, 1451 (1915). Richards and Lewis, *Proc. Am. Acad.*, **34**, 87 (1898). Richards, Wilson and Garrod-Thomas, *Carnegie Inst. Pub.*, **118**, 1 to 72 (1909). Richards and Daniels, *Trans. Am. Electrochem. Soc.*, **22**, 343 (1912); *THIS JOURNAL*, **41**, 1732 (1919).

A fairly complete historical account of the earlier work is found in the paper by Richards and Forbes, *Carnegie Inst. Pub.*, **56**, 1 (1906). This has been brought up to 1918 in the thesis presented for the doctor's degree to the Faculty of Arts and Sciences of Harvard University by Farrington Daniels, June, 1918.

<sup>2</sup> Meyer, *Wied. Ann.*, **40**, 244 (1890). Cady, *J. Phys. Chem.*, **2**, 551 (1898); with correction, **3**, 107 (1899). Schoeller, *Z. Elektrochem.*, **5**, 259 (1898). Haber and Sack, *ibid.*, **8**, 245 (1902). Lewis and Kraus, *THIS JOURNAL*, **32**, 1459 (1910).

### The Preparation of Substances

After several rather unsuccessful attempts, the method of preparing the sodium amalgams from mercury and the solid metal used by Lewis and his collaborators<sup>3</sup> and MacInnes and Parker<sup>4</sup> was rejected as inconvenient and the amalgam was prepared by electrolysis.<sup>5</sup> A saturated solution of pure sodium carbonate (four times recrystallized and centrifuged) was electrolyzed in a cell consisting of an ample mercury cathode and an anode of platinum foil; a wide-mouthed half-liter bottle served as the container. After passing a current of 4 amperes for a few hours, the amalgam became pasty and the process was stopped. The electrolyte was poured off as completely as possible and the amalgam was thoroughly agitated with 4 or 5 fresh portions of distilled water and subsequently with 2 portions of alcohol. It was transferred to a small flask which was evacuated and heated for some minutes. Having been thus dried, it was placed while still hot in a desiccator where it remained until it was diluted, filtered through a capillary tube (which eliminated the film of hydroxide) and transferred directly to the electrodes, as described below.

The sodium hydroxide solution used as electrolyte in the measuring cells was prepared from pure sodium amalgam and water, the action being hastened by making the amalgam the anode in a suitable cell. This solution was approximately 0.5 N.

Mercury was purified by repeatedly dropping it in a fine stream through a solution of mercurous nitrate and nitric acid. It was subsequently distilled in a current of air and then in a current of pure hydrogen.

Hydrogen was prepared by the electrolysis of dil. sodium hydroxide solution, and was passed through a tower of glass beads covered with sodium hydroxide solution, through a hot tube containing platinized asbestos, over solid potassium hydroxide and finally over phosphorus pentoxide.

### The Cell and Its Manipulation

The cell previously used by one<sup>6</sup> of us could not be used in this research because of the rapid action between sodium amalgam and aqueous solutions. There were two alternatives,—either to work in an anhydrous medium or to use an aqueous electrolyte and circumvent the action of the amalgam on the water by the use of a special form of electrode. The first alternative had been chosen by Cady and Haber, the second by Meyer, Schoeller, and MacInnes and Parker, while Lewis used both methods.<sup>7</sup> To us the second alternative seemed to be the most convenient. Lewis's

<sup>3</sup> G. N. Lewis and Kraus, Ref. 1.

<sup>4</sup> MacInnes and Parker, *THIS JOURNAL*, 37, 1451 (1915). They prepared potassium not sodium amalgam.

<sup>5</sup> After this method had been elaborated, Lewis, Adams and Lanman published a somewhat similar method, having abandoned the earlier process. *THIS JOURNAL*, 37, 2856 (1915).

<sup>6</sup> Richards and Forbes, *Carnegie Inst. Pub.*, 56 (1906).

<sup>7</sup> Lewis and Kraus, Ref. 1.

electrode was consequently taken as a model; numerous modifications of it were tried before a satisfactory apparatus was obtained.

We found that the cell must meet the following requirements: (1) each amalgam should be measurable against several other amalgams; (2) each amalgam should be held in a protecting container, which should always deliver an amalgam of the same composition for potential measurements and for analysis; (3) the two amalgam surfaces between which the potential is being measured should be constantly changing, and the movements of the two surfaces should be as nearly as possible synchronous.

These specifications were fulfilled by a cell composed of two electrodes constructed as shown in the accompanying illustration.

Each electrode (Fig. 1) had its own reservoir of amalgam and was provided with a side-tube B and a leveling bulb A containing mercury which ensured sufficient pressure to cause the amalgam to flow out when desired. The capillary tube D was likewise filled with the amalgam, electrical contact being made by means of a sealed-in platinum wire and a side-tube E containing mercury. The shape of the orifice is of great importance, since with an ordinary opening there is a tendency for the amalgam to recede after each drop has been ejected, thereby drawing in small amounts of the electrolyte and also greatly changing the resistance of the cell. An excellent aperture (see Fig. 2) was obtained by allowing the end of the capillary tube to fall together in a flame and subsequently grinding away the glass until the top of the arch-shaped cavity was reached. A file-scratch was cut in each stopcock in the usual way, thus allowing the rate of egress of the amalgam to be easily and accurately adjusted. The stopcock was not greased in the middle, in order to avoid contaminating the amalgams.

Each electrode was filled in the following manner. Clamped horizontally and sealed to a larger glass vessel [(A) Fig. 3] by means of a 0.2 mm. capillary tube (C), it was dried when warm by a current of very dry air drawn through the apparatus for 20 minutes. The desired amalgam was next introduced through B into the large reservoir (A). This amalgam had been prepared by suitably diluting with pure mercury some of the semi-solid electrolytic amalgam, rough analyses having determined approximately the desired concentration. After the introduction of the amalgam through B into A, the whole system was attached to a pump at B and alternately evacuated and filled with pure hydrogen and finally partially evacuated. The electrode system was now turned through  $180^\circ$  around a lengthwise horizontal axis and slightly inclined, the amalgam thus collecting in one end of A. By allowing hydrogen to enter at B, the amalgam was forced through the capillary tube C into the reservoir of the electrode, thus being filtered from its film of hydroxide. When the electrode

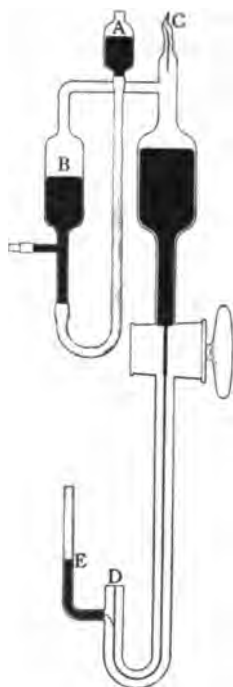


Fig. 1.—A single electrode, the amalgam being placed in C.

reservoir was full, the capillary tube was sealed off, the electrode returned to its normal vertical position, the apparatus filled with hydrogen through the projecting side-tube and mercury run into the leveling bulb. The capillary tube was next exhausted, dried, and completely filled with amalgam.

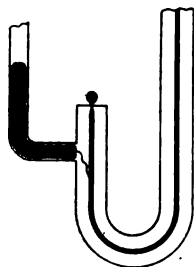


Fig. 2.—Detail of single electrode tip.

For the determination of the difference between their electromotive effects, two such electrodes were supported side by side in such a manner that the apertures at the ends of the capillary tubes were as close together as possible and about a centimeter below the surface of the electrolyte of pure sodium hydroxide solution which was contained in a half-liter beaker. Hydrogen was bubbled through the electrolyte, thus keeping it stirred and free from dissolved air. The temperature of the thermostat employed was held constant within  $0.005^{\circ}$ .

Lewis and Jackson,<sup>8</sup> Walker,<sup>9</sup> Baker<sup>10</sup> and others have shown the great influence of traces of impurities upon the speed of reaction between water and sodium amalgam. By preparing pure sodium amalgam and pure sodium hydroxide it was hoped that this action might be made as slow as possible.

Preliminary measurements showed that when fresh globules of amalgam were allowed to form at each electrode and the surfaces then kept stationary, the potential between them was not constant for any length of time, but steadily increased. With amalgams containing more than 0.1% of sodium this increase was not more than 0.1 mv. in 5 or 10 minutes; but for more dilute amalgams the increase was so rapid that reproducible results with stationary electrodes could not be obtained. This

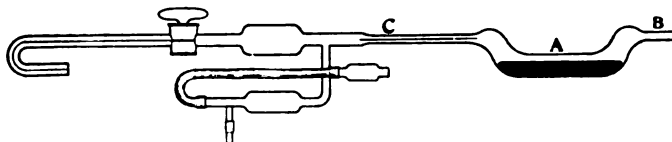


Fig. 3.—Method of filling electrode.

must be due to a greater percentage loss of sodium on the surface of dilute than on the surface of concentrated amalgams. In other words, the losses in sodium were more nearly identical in each case than were the original concentrations. Since the potential of the cell is a function of the ratio of the two concentrations, subtracting a nearly equal amount from both concentrations will increase the value of the ratio and consequently the observed electromotive force.

To obviate this change in potential and to enable the method to be used with amalgams of all concentrations, a device shown in Fig. 4 was

<sup>8</sup> Lewis and Jackson, *Proc. Am. Acad.*, 41, 403 (1906).

<sup>9</sup> J. W. Walker and Paterson, *Trans. Am. Electrochem. Soc.*, 3, 185 (1903).

<sup>10</sup> Baker and Parker, *J. Chem. Soc.*, 103, 2060 (1913).

employed. A glass rod was bent and supported in such a way that it could be moved across the tops of the capillary tubes simultaneously, brushing off the two globules of amalgam. In determining the electromotive force of the cell the stopcocks were turned so that the amalgams slowly issued at about the same rate from their respective openings. After the glass arm had moved across, brushing a way the drops which were forming, the subsequent drops on each electrode started at the same moment and formed at approximately the same rate. If the potential was measured during this time, a definite, constant electromotive force of the cell could be determined. Only by the use of this method could consistent and reproducible results be obtained with the very dilute amalgams. When the amalgams were allowed to drop slowly from the electrode and the potential was determined

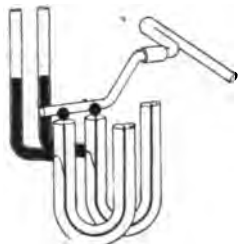


Fig. 4.—The details of two electrodes with arrangement for the removal of exuding drops synchronously.

without the aid of the arm, the results varied appreciably. This was probably due to the fact that unless the drops on each electrode started at the same moment, a comparatively large old surface might be measured against a small new one. That the results obtained by this method are much better than results from standing or irregular drops is clear. Whether with the most dilute amalgams the results were wholly free from error due to solution of sodium is uncertain. In the case of the most concentrated, more safely measured, amalgams the values obtained were identical with potentials measured with a stationary surface, and are probably to be depended on within 0.05 mv. Moreover, it will be shown later that the results were thermodynamically consistent.

### The Analysis of the Amalgams

The method of analysis employed was in principle that employed in 1913 by one of us in collaboration with F. Daniels in the case of thallium,<sup>11</sup> and independently recommended by Lewis<sup>12</sup> in his recent paper on "The Electrical Transference in Amalgams."

After the rejection of the first 10 or 12 drops of amalgam (for obvious reasons, if the apparatus had been quiet for any considerable time) about 10 g. was run from the electrode into a previously weighed Erlenmeyer flask, which was then reweighed. A little more than the needed approximately known quantity of standardized 0.01667 *N* hydrochloric acid was run into the flask, which was again weighed, and the flask was stoppered and thoroughly shaken. Shaking was stopped as soon as the mercury broke up into minute permanent globules, showing complete extraction of the sodium.<sup>11</sup>

<sup>11</sup> Richards and Daniels, *THIS JOURNAL*, 41, 1736 (1919). The publication was delayed by the war.

<sup>12</sup> Lewis, *ibid.*, 37, 2656 (1915).

The contents of the flask were now titrated with 0.0025 *N* barium hydroxide solution, the solution being stirred with a current of air free from carbon dioxide. Rosolic acid, used as the indicator gave an end-point within 0.1 cc. of hydroxide (or 0.00005 g. of sodium). Thus by using a 10 g. sample, an amalgam containing only 0.01% of sodium could be analyzed with an accuracy of about 0.5%. The barium hydroxide was standardized against carefully prepared 0.01 *N* oxalic acid. Duplicate analyses of amalgams (never more different than 0.5% and usually within 0.1%) were always made.

### The Measurement of Electromotive Force

The potentiometer was a recent model Wolff instrument of the best quality. Actuated by two large dilute cadmium cells (according to Hulett), it was standardized by a number of other carefully prepared Weston cells (taken as 1.0184 volt  $-0.00004$  ( $t - 20^\circ$ ) volt) and used with a sensitive Leeds and Northrup d'Arsonval galvanometer. Incidentally, the potentiometer was compared with that used in the earlier work on thallium amalgams, and the two were found to give identical values (within a reasonable very small limit of error) for several zinc amalgam cells. Thus the two instruments mutually confirmed one another.

The potential of each sodium amalgam cell was determined by a series of approximations. The potentiometer having been set at nearly the potential to be measured, the amalgams were allowed to flow, and immediately after the electrode surfaces had been brushed with the arm, the galvanometer circuit was closed and the deflection noted. This procedure was repeated until two settings of the potentiometer were found that caused equal but opposite deflections of the galvanometer; the true electromotive force was taken as the mean of these two readings, which were usually about 0.00005 volt apart. To secure exact results the galvanometer circuit must be closed at the moment when fresh globules simultaneously start to form on both electrodes.

### Summary of Results

The potentials of all the cells which were measured satisfactorily at  $25^\circ$  according to the procedure as described above are given in Table I. Three preliminary electrodes (6, 8, 12) containing very dilute amalgam, and measured before the technique for dilute amalgams had been mas-

TABLE I  
MEASUREMENTS OF E.M.F. AT  $25.00^\circ$   
For the concentrations of the various amalgams see Table III

Cell composed of electrodes Nos.	E.m.f. at $25.0^\circ$ Mv.	Cell composed of electrodes Nos.	E.m.f. at $25.0^\circ$ Mv.
4-5	52.58	16-17	4.99
7-5	36.10	15-17	14.73
9-10	56.45	18-19	57.14
13-11	33.80	19-16A	46.36
13-14	42.18	18-16A	103.50
14-15	12.82	18-20	35.77
13-15	54.93	20-21	53.12
15-16	9.74	21-22	19.43

tered, were rejected. They gave values 1.5 mv. greater than Nos. 17 and 22.

The consistency of the results was confirmed in the usual way by comparing the values of three electrodes measured in pairs. Typical results are given below. In no case was the difference between the sum of A—B and B—C, and the observed value of A—C greater than 0.08 mv., and it was usually less than 0.05.

TABLE II  
COMPARISON OF VALUES  
E.m.f. in millivolts

Electrode Nos.	I A → B	II B → C	III A → C	IV Sum I + II	Difference III—IV
15, 14, 13	12.82	42.18	54.93	55.00	-0.07
17, 16, 15	4.99	9.74	14.73	14.73	-0.00

From the values in Table I a consistent table of all the electromotive forces may obviously be built up in the usual way, basing all upon the most concentrated amalgam.<sup>13</sup> These values ( $\pi_2$ ) are given in the fifth column of Table III, the concentrations of each amalgam being recorded in the second column of this table. The fourth column gives the potentials which would have been observed if the simple thermodynamic concentration-equation

$$\pi_1 = \frac{RT}{F} \ln \frac{V_2}{V_1}$$

were fulfilled.

TABLE III  
ELECTROMOTIVE FORCES

Electrode No.	Na in amalgam %	$V_1/\pi_1$ , or dilution in terms of No. 9	Potential if No. 9 = 0 Calc. $\pi_1$	Obs. $\pi_2$	$\Delta\pi$ Difference
9	0.551	.....	.....	.....	.....
18	0.416	1.323	7.18	17.15	9.97
4	0.393	1.403	8.68	20.63	11.95
7	0.2895	1.903	16.51	37.11	20.60
20 <sup>a</sup>	0.1978	2.790	26.32	[52.92] <sup>a</sup>	[26.60] <sup>a</sup>
13 <sup>a</sup>	0.1862	2.960	27.83	[55.54] <sup>a</sup>	[27.70] <sup>a</sup>
10	0.1815	3.035	28.47	56.45	27.98
5	0.1174	4.69	39.65	73.21	33.56
19	0.1102	5.00	41.30	74.29	32.99
11	0.0707	7.795	52.69	89.34	36.65
14	0.0533	10.33	59.89	97.65	37.76
21	0.0396	13.90	67.51	106.04	38.53
15	0.0344	16.00	71.12	110.47	39.35
16	0.0240	22.98	80.41	120.20	39.79
16A	0.0236	23.35	80.83	120.65	39.82
17	0.0200	27.55	85.07	125.20	40.13
22	0.0197	27.95	85.45	125.47	40.02

<sup>a</sup> The values for  $\Delta\pi$  for electrodes Nos. 13 and 20 were found by interpolation from the other results;  $\pi_2$  was then found by adding  $\Delta\pi$  and  $\pi_1$ .

<sup>13</sup> See Ref. 6, pp. 35, 43.



The figures in the last column of the foregoing table, which give the differences ( $\Delta\pi$ ) between the observed potentials ( $\pi_2$ ) and the theoretical but obviously inadequate concentration effects ( $\pi_1$ ) are at first more than half the observed value, the deficiency of the theoretical e.m.f. being almost exactly half the observed value between concentrations 0.55 and 0.19% by weight (or 4.7 and 1.65 atom-per cent.) This deficiency is considerably larger even than in the case of thallium,<sup>14</sup> where the deficiency of the theoretical e.m.f. for a similar atom-per cent. relation was only about one-quarter instead of only half of the observed value. Evidently where great affinities are involved, as in the case of sodium and mercury, the concentration law is a very poor guide to potential. This matter will be considered in detail later.

The observed values were plotted in the accompanying diagram, (Fig. 5), by first laying down 9, and 10, then 4 to 12, and finally placing 13 on the curve of the first series in a locus determined by its concentration. This is the graphic equivalent of the method used in constructing Table III. Evidently the results are very consistent: The points form a smooth and

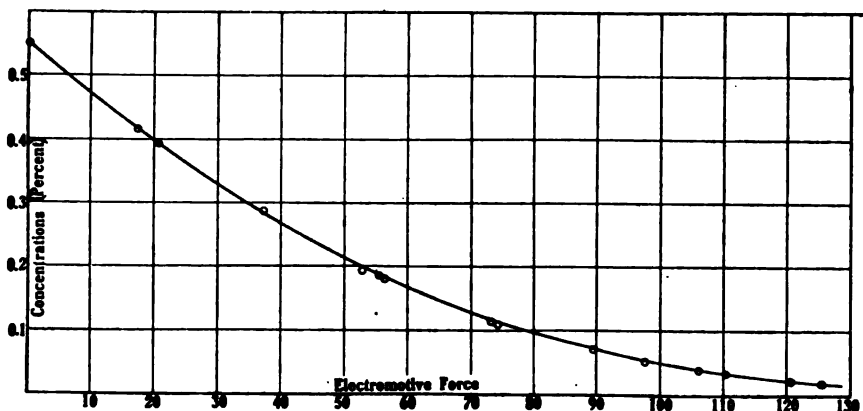


Fig. 5.—Graph of electromotive force between amalgams.

continuous curve. On the whole they seem to be quite as good as could be expected in an aqueous electrolyte with so reactive a substance as sodium amalgam.

On comparing these results with the few earlier values obtained by Meyer<sup>2</sup> and by Cady,<sup>2</sup> a fair degree of agreement between them all is found, although at the time the early values appeared to be mutually inconsistent. Cady's two cells gave potentials of 91 and 95 millivolts, respectively, whereas our corresponding values (found from the curve) are 93.5 and 99.8 respectively. Meyer's single crude measurement gave 12 instead of our estimate 17.4.

<sup>14</sup> Richards and Daniels, Ref. 11, p. 1740. Amalgams B and D.

### The Temperature Coefficients

The temperature coefficients of 4 cells were determined by measuring their electromotive forces at 15°, 25°, and 35°. By making all the measurements on each cell within a few hours, possible errors due to changes

TABLE IV  
EFFECT OF TEMPERATURE ON E.M.F.

Electrodes Nos.	Electromotive force of the cell in millivolts			$\Delta\pi/\Delta T$		Average
	15°	25°	35°	15-25°	25-35°	
18-20	34.84	35.77	36.67	0.156	0.154	0.155
18-19	55.82	57.38*	58.92	0.093	0.090	0.0915
20-21	51.48	53.12	54.73	0.164	0.161	0.1625
21-22	18.84	19.43	20.05	0.059	0.063	0.061

\* A different value from that given in Table I. The measurements above were made some days later, Amalgam 19 having slightly changed in concentration.

in concentration of the amalgams were avoided. The agreement between the value of the temperature coefficient as calculated from 15° to 25° and from 25° to 35° was satisfactory, and affords further evidence of the accuracy of all the results. Table IV records the measurements.

That these values of  $\Delta\pi/\Delta T$  are much smaller than those demanded by the perfect gas law is shown by the following table, which gives  $\frac{\Delta\pi}{\pi_{25^\circ}\Delta T}$ , a quantity which should equal 0.003355 if the perfect gas law held in the mercurial solution.

TABLE V  
RATIO OF TEMPERATURE COEFFICIENTS TO POTENTIAL

Sodium in first amalgam C <sub>1</sub> %	Sodium in second amalgam C <sub>2</sub> %	Average Value of $\Delta\pi/\Delta T$	$\frac{\Delta\pi}{\pi_{25^\circ}\Delta T}$
0.416	0.1978	0.0915	0.00260
0.416	0.1102	0.155	0.00264
0.1978	0.0396	0.1625	0.00306
0.0396	0.01972	0.061	0.00314

Evidently the temperature coefficient approaches perfect regularity as dilution increases; at the point where the potential itself corresponds to the concentration law, the temperature coefficient would doubtless equal that required by the law of Charles.

### The Helmholtz Equation and the Heat of Transfer of Sodium

Aside from a few rough experiments of Berthelot<sup>15</sup> and a few more of Cady<sup>2</sup> on heats of dilution, there has been no thermochemical study of sodium amalgams. It has been shown that these data are not directly applicable to the thermodynamic consideration of the electrochemical results, because the latter involve not dilution, but rather transfer of

<sup>15</sup> Berthelot, *Ann. chim. phys.*, [5] 18, 442 (1879).

sodium from a more concentrated to a more dilute amalgam.<sup>16</sup> The total energy change involved in this latter process may, of course, be calculated from the Helmholtz equation using the results tabulated above; in this case it is practically equal to the change in heat content. The following table records the values of

$$U = n\pi F - nFT \frac{\Delta\pi}{\Delta T}$$

TABLE VI  
TOTAL ENERGY CHANGE

C <sub>1</sub> %	Sodium C <sub>2</sub> %	$\pi$ , <sup>a</sup>	$\Delta\pi/\Delta T$	$\pi/F$	$FT \frac{\Delta\pi}{\Delta T}$	$U$ in joules
0.416	0.1978	0.03577	0.0000915	3451	2632	819
0.416	0.1102	0.05738	0.000155	5540	4459	1081
0.1978	0.0396	0.05312	0.0001625	5129	4674	455
0.0396	0.01972	0.01943	0.000061	1875	1755	120

These values have been confirmed by actual measurements of the heat of dilution of amalgams, which will be recounted in a later paper.

As would be expected the heat of transfer ( $U$ ) decreases rapidly with increasing dilution. With concentrated solutions the amount of heat evolved is greater than for equivalent proportions (on the gram atom basis) of the other amalgams investigated in this laboratory. The amount of heat evolved in the transfer of a gram atom of thallium<sup>17</sup> over the range corresponding to the first of the above cells is not over 650 joules instead of 819.

In 1898 Cady<sup>2</sup> proposed the following equation,

$$\pi = \frac{RT}{nF} \ln \frac{C_1}{C_2} + \frac{U}{nF}$$

This can be true only when the simple concentration law holds for the osmotic part of the effect, and when no change of heat capacity occurs.<sup>18</sup> When combined with the Helmholtz equation, it gives the following relationship,

$$\frac{R}{nF} \ln \frac{C_1}{C_2} = \frac{\Delta\pi}{\Delta T}$$

an expression which gives a method of testing the Cady equation without determining  $U$ .<sup>19</sup> A comparison of the two members of the above equation taken from the foregoing data is given in Table VI. Obviously in all cases except the most dilute solution the two members show considerable lack of equality. This is probably due chiefly to failure of the concentration law, but perhaps partly to the effect of changing heat capacity.

<sup>16</sup> Ref. 11, p. 1761.

<sup>17</sup> Ref. 11, p. 1760. The value is taken from the curve.

<sup>18</sup> Richards, *Z. physik. Chem.*, **42**, 145 (1902); *Proc. Am. Acad.*, **38**, 308 (1902).

<sup>19</sup> Richards, Wilson and Garrod-Thomas, Ref. 1, p. 59.

Here again the concentration law gives too small quantities. We are inclined to accept the often suggested explanation of hydrargyration of the dissolved sodium.

TABLE VII  
CONCENTRATION EFFECT AND TEMPERATURE COEFFICIENTS

$C_1$	$C_2$	$C_1/C_2$	$\frac{R \ln C_1/C_2}{F}$	$\frac{\Delta \pi}{\Delta T}$
0.416	0.1978	2.109	0.0642	0.0915
0.416	0.1102	3.780	0.1145	0.1550
0.1978	0.0396	4.990	0.1380	0.1625
0.0396	0.01972	2.010	0.0600	0.0610

Further theoretical considerations are postponed until the thermochemical data are ready for publication.

We are greatly indebted to the Carnegie Institution of Washington for much of our apparatus.

### Summary

1. Improvements have been effected in the electrolytic preparation and the subsequent manipulation of pure liquid sodium amalgam, as well as in the apparatus for the measurement of the electromotive force of sodium amalgam concentration cells with aqueous electrolyte.

2. The electromotive forces of many concentration cells of liquid sodium amalgam have been measured at 25° and a few cells also at 15° and 35°.

3. The deviations of these potentials from the simple concentration-law were found to be greater in sodium amalgam than with any other mercurial solution hitherto studied in detail.

4. The heats of transfer of sodium from one amalgam to another calculated by the Helmholtz equation, are found to be unusually large.

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### NOTES

**The Rapid Analysis of Potassium Perchlorate.**—In reviewing the various methods proposed for the analysis of potassium perchlorate, it is noted that the only principle that has been successfully applied is that of heating the perchlorate, either alone or mixed with some other substance. In the practical application of the principle the loss by volatilization of the resulting potassium chloride is the greatest source of error.

The method of heating the perchlorate with manganese dioxide has given such satisfactory results that it has been thought worth while to record the procedure.

A 0.5g. sample of potassium perchlorate is intimately mixed in an agate mortar with 1.0 g. of manganese dioxide. The charge is transferred to a porcelain crucible and heated for 15 minutes at a temperature of 600–

700°. After cooling, the mass is extracted with hot water, filtered, and the chlorine determined by either Mohr's or Volhard's method. The results obtained average about 0.2 to 0.3% low, indicating a small loss by volatilization, but are sufficiently accurate for most purposes. Should greater accuracy be desired, the method of Lamb and Marden<sup>1</sup> of heating the perchlorate alone in a glass test-tube and retaining the fumes evolved with a plug of asbestos wool, may be employed. When manganese dioxide is used, a blank is necessary inasmuch as commercial as well as native manganese dioxide always contains a small amount of chlorine.

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### **Electrolytic Reduction of Chromic Chloride to the Divalent Salt.<sup>1</sup>**

The problem of chromium reduction arose in connection with the work done at the Edgewood Laboratory on a method for producing ethylene from acetylene by the use of a solution of chromous chloride as a reducing agent. It was proposed to convert the chromic chloride produced by the acetylene treatment back to the divalent salt by means of electrolytic reduction. The investigations described in the present communication were undertaken to find conditions whereby it would be possible to obtain satisfactory yields of chromous chloride.

In the electrolytic reduction of chromic to chromous chloride the principal source of inefficiency is the production of hydrogen gas at the cathode. In some of our preliminary attempts at reduction an insoluble deposit formed on the cathode. The formation of such a coating of course represented inefficiency as far as the production of chromous chloride was concerned. However, the conditions under which the experiments reported herewith were carried out were such as to prevent the formation of any such deposit, and we may therefore regard the production of hydrogen gas as the only source of inefficiency in these particular experiments. Just what caused the deposit to appear in the preliminary work is unknown, but it may have been due to impurities in the chromic chloride solution, or to too high current density when the chromic concentration of the solution became small.

The following procedure was adopted as a means of determining the part of the current used for reduction purposes: the hydrogen evolved from the cathode in a given time and by a known amount of current was measured and reduced to standard conditions; the total hydrogen which would have been evolved by the current, had none of it been used for reduction pur-

<sup>1</sup> Lamb and Marden, *THIS JOURNAL*, **34**, 812 (1912).

<sup>1</sup> Published by permission of General Amos Fries, Chief of the Chemical Warfare Service.

poses, was calculated from the known current amperage; the difference between this volume and the volume actually evolved represented the amount used in reducing chromic chloride and was a measure of the efficiency. The results obtained by this procedure were found to check those obtained by determining the chromous chromium produced by a given amount of current.

The reduction was carried out in an ordinary 2-compartment cell, with a spiral spongy lead cathode surrounded by 5 graphite anodes. The 2 compartments were separated by a porous cup of rather fine structure. In order to obtain the best results it was found essential to provide for a stirrer in the cathode compartment.

Numerous experiments were performed with results similar to those reported in Table I. The efficiency was good at the beginning of the reduction when the concentration of chromic chromium was high, but as this was consumed the efficiency fell off rapidly. In some experiments where the reduction was carried on until 86% of the chromium was reduced, only 9% of the current was being used to reduce the remaining chromic chromium.

It seemed that the efficiency might be a linear function of the chromic-ion concentration. In order to prove this the action was assumed to be that of nascent hydrogen produced by the current at the cathode on trivalent chromium, thus,  $\text{Cr}^{+++} + \text{H} \longrightarrow \text{Cr}^{++} + \text{H}^+$ . When hydrogen gas was being given off at the cathode even in small quantities we have assumed that the concentration of nascent hydrogen was constant and at its maximum. If this is true and if the reaction proceeds as indicated, the rate of reduction would be proportional to the concentration of chromic chromium, thus,  $\frac{dx}{dt} = K(a-x)$ , where  $x$  is the amount of chromous chromium formed in  $t$  minutes, and  $a$  is the original concentration of trivalent chromium. Beginning at the point where appreciable inefficiency appeared, the  $K$  value in the above equation was calculated from the data of Table I and tabulated in the column marked  $K$ . In the same way calculations were made on several other experiments, all of which indicated that the rate of reduction was a linear function of the chromic chromium concentration.

Now, if we bring this theory to bear on the problem of securing high efficiency, we see at once that the reduction will theoretically proceed as fast when we have only a small excess of hydrogen as when there is a large excess. In other words, the rate of reaction as determined by the concentration of trivalent chromium prevents the use for reduction purposes of more than a certain amount of current at any given time, and if we use more than this we are certain to decrease the efficiency. The current employed then may be very high at first, but should be decreased during reduction in proportion to the decrease in chromic concentration.

TABLE I  
REDUCTION EMPLOYING CONSTANT CURRENT DENSITY  
Volume of cathode solution at start, 225 cc.  
Grams of Cr per cc., 0.11031  
Grams of Cr<sup>++</sup> per cc., 0.00128  
Total cathode surface, 1.24 sq. dm.

Time	Amperage	Hydrogen evolved Cc.	Total hydrogen Cc.	Efficiency %	Cr as Cr <sup>++</sup> %	K
9.47-11.05	1.6	0.0	...	100.0	17.4	....
11.05-11.35	1.6	0.4	334.1	99.9	23.6	....
11.35-12.05	1.6	0.7	334.1	99.8	29.9	....
12.05-12.35	1.6	0.9	334.1	99.7	36.1	....
12.35- 1.05	1.6	7.5	334.1	97.8	42.2	0.00335
1.05- 1.35	1.6	34.2	334.1	89.8	47.8	0.00338
1.35- 2.05	1.6	68.4	334.1	79.5	52.8	0.00336
2.05- 2.35	1.6	97.5	334.1	70.8	57.2	0.00334
2.35- 3.05	1.6	115.8	334.1	65.3	61.3	0.00334

Several experiments according to this method have shown that by reducing the amperage to correspond with the decrease in chromic chromium, an efficiency of 96% can be maintained over the period required to reduce 87% of the chromium; whereas, by holding the amperage constant only 53% efficiency could be obtained for the same amount of reduction.

The authors wish to acknowledge the help and suggestions received from members of the staff at the Edgewood Laboratory, and especially from Capt. R. E. Hall, in charge of the Physical Chemistry Division.

CONTRIBUTION FROM THE CHEMICAL LABORATORY  
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Received October 17, 1921

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF PITTSBURGH]  
**COMPOUNDS OF TELLURIUM TETRABROMIDE WITH ORGANIC BASES<sup>1</sup>**

BY ALEXANDER LOWY AND RAYMOND F. DUNBROOK<sup>2</sup>

Received September 17, 1921

This investigation was undertaken with a twofold purpose in view: (1) to prepare compounds of tellurium tetrabromide with organic bases which will be utilized in further research work, and (2) to prepare selenium and tellurium dyes analogous to the class of sulfur dyes by substituting the element selenium or tellurium in place of sulfur, as, for example, in the preparation of sulfur black, etc.

<sup>1</sup> Presented before the Division of Organic Chemistry of the American Chemical Society, New York, September 6-9, 1921.

<sup>2</sup> This report represents an abstract of a thesis presented by R. F. Dunbrook, in partial fulfilment of the requirements for the degree of Master of Science, September, 1921.

Rust<sup>3</sup> investigated the action of tellurium tetrachloride on phenols and phenol ethers and found that complexes of the type  $\text{TeCl}_4(\text{C}_6\text{H}_4\text{-OCH}_3)_2$  and  $\text{TeCl}_4(\text{C}_6\text{H}_5\text{.OH})_2$  were formed.

Lenher<sup>4</sup> has tried the action of tellurium tetrachloride and of tellurium tetrabromide on amines. When tellurium tetrachloride or tellurium tetrabromide, dissolved in the corresponding halogen acid, is added to an amine, also dissolved in the corresponding halogen acid, complexes of the type  $(\text{C}_6\text{H}_5\text{NH}_2\text{HBr})_2\text{.TeBr}_4$ , are formed in which two moles of the salt of the amine are combined with one mole of tellurium tetrabromide. The tellurium tetrabromide is prepared by dissolving tellurium dioxide in hydrobromic acid.

In the course of this investigation, it was found that when pure tellurium tetrabromide is dissolved in absolute ether or in glacial acetic acid, and a solution of a primary, secondary or tertiary aromatic amine, or a substituted amine is added to the solution, yellow or orange colored precipitates are formed which are the addition products of tellurium tetrabromide and the amines. It was further found that the number of moles of the amine that were combined with one mole of tellurium tetrabromide depended upon the number of amino groups in the molecule. If one amino group was present in the molecule, then two molecules of the amine combined with one mole of tellurium tetrabromide. When two amino groups were present in the molecule, then the ratio was one mole of the amine to one mole of tellurium tetrabromide. A list of compounds prepared is given under Experimental Part.

### Experimental Part

The pure tellurium tetrabromide was prepared as described by Hauer<sup>5</sup> and was recrystallized from acetic acid.

The data following contain the essential results obtained.

Name of product and formula	Color and form	Solvents	Ratio of amine to $\text{TeBr}_4$	Calc. %	Analysis Found %
Bis-aniline tellurium tetrabromide $(\text{C}_6\text{H}_5\text{NH}_2)_2\text{.TeBr}_4$	yellow amorphous	ether	2:1	Te, 20.13 Br, 50.47	20.09, 20.33 50.26, 50.53
Bis- <i>p</i> -bromo-aniline tellurium tetrabromide $(\text{BrC}_6\text{H}_4\text{NH}_2)_2\text{.TeBr}_4$	yellow amorphous	acetic acid	2:1	Te, 16.11 Br, 60.59	16.00, 15.99 60.63, 60.44
Bis-diphenylamine tellurium tetrabromide $[(\text{C}_6\text{H}_5)_2\text{NH}]_2\text{.TeBr}_4$	orange needles	acetic acid	2:1	Te, 16.23 Br, 40.69	16.25, 16.26 40.17, 40.94

<sup>3</sup> Rust, *Ber.*, 30, 2828 (1897).

<sup>4</sup> Lenher, *THIS JOURNAL*, 22, 136 (1900).

<sup>5</sup> Hauer, *J. prakt. Chem.*, 73, 98 (1858).



Name of product and formula	Color and form	Solvents	Ratio of amine to TeBr <sub>4</sub>	Calc. %	Analysis Found %
Bis-dimethylaniline tellurium tetrabromide $[\text{C}_6\text{H}_5\text{N}(\text{CH}_3)_2]_2 \cdot \text{TeBr}_4$	orange needles	acetic acid	2:1	Te, 18.49 Br, 46.36	18.51, 18.79 46.32, 46.56
Bis- $\beta$ -naphthylamine tellurium tetrabromide $(\text{C}_{10}\text{H}_7\text{NH}_2)_2 \cdot \text{TeBr}_4$	orange needles	acetic acid	2:1	Te, 17.38 Br, 43.53	17.58, 17.21 43.63, 43.71
<i>p</i> -phenylenediamine tellurium tetrabromide $\text{C}_6\text{H}_4(\text{NH}_2)_2 \cdot \text{TeBr}_4$	yellow amorphous	acetic acid	1:1	Te, 22.96 Br, 57.57	22.60, 22.57 57.70, 57.54
<i>m</i> -tolylenediamine tellurium tetrabromide $\text{C}_7\text{H}_6(\text{NH}_2)_2 \cdot \text{TeBr}_4$	yellow amorphous	acetic acid	1:1	Te, 22.40 Br, 56.15	22.70, 22.44 56.12, 56.71
Benzidine tellurium tetrabromide $\text{H}_2\text{NC}_6\text{H}_4 \cdot \text{C}_6\text{H}_4\text{NH}_2 \cdot \text{TeBr}_4$	yellow amorphous	acetic acid	1:1	Te, 20.19 Br, 50.63	20.46, 20.24 50.88, 50.59
Tetramethyl-diamino-phenylmethane tellurium tetrabromide $(\text{CH}_3)_2\text{NC}_6\text{H}_4 \cdot \text{CH}_2 \cdot \text{C}_6\text{H}_4\text{N}(\text{CH}_3)_2 \cdot \text{TeBr}_4$	yellow amorphous	acetic acid	1:1	Te, 18.18 Br, 45.57	18.21, 18.51 45.76, 45.73

The compounds described in the table were prepared by mixing solutions of the amines and of tellurium tetrabromide in the ratios given, in ether or in glacial acetic acid. The yield in all cases was practically quantitative.

The bases are all yellow amorphous powders, but those that can also be prepared crystalline have an orange color. They are stable in the air, but water and alcohol readily decompose them with the formation of tellurous acid. They have no melting points and decompose when heated above 100°. The bases described are insoluble in absolute ether, chloroform, carbon tetrachloride, carbon disulfide, benzene, toluene, petroleum ether, acetone and in glacial acetic acid. Dilute acids readily dissolve them.

When bis-aniline tellurium tetrabromide is dissolved in dil. hydrobromic acid and recrystallized twice from the same solvent, the base forms a new complex, consisting of four moles of aniline hydrobromide combined with one mole of tellurium tetrabromide.

Subs., 0.2110, 0.3850. Calc. for  $(\text{C}_6\text{H}_5\text{NH}_2\text{HBr})_4 \cdot \text{TeBr}_4$ : Te, 11.15. Found: 11.13, 10.91.

Subs., 0.1844, 0.2600. Calc. for  $(\text{C}_6\text{H}_5\text{NH}_2\text{HBr})_4 \cdot \text{TeBr}_4$ : Br, 55.92. Found: 55.62, 55.75.

The other bases form analogous products with hydrobromic acid.

Alkaloids such as brucine and quinine also give yellow amorphous precipitates with tellurium tetrabromide.

Experiments were conducted to prepare selenium and tellurium dyes analogous to the sulfur dyes obtained in processes which employ the element sulfur. The conclusions from our experiments seem to be that, in the preparation of selenium and tellurium dyes, compounds of selenium and tellurium would have to be used instead of the elements themselves. It seems that under conditions similar to those which hold for sulfur, selenium and tellurium do not form dyes.

When selenium or tellurium was suspended in concentrated solutions of sodium hydroxide, together with various organic compounds, such as dinitrophenol, diphenylamine, and *p*-phenylenediamine, and the mixtures were refluxed, no color formation seemed to take place, although in some experiments, the mixtures were refluxed for 100 hours. The temperatures ranged from 100–120°.

It seemed probable that if selenium or tellurium were fused with sodium hydroxide or sodium carbonate,  $\text{Na}_2\text{Se}_n$  or  $\text{Na}_2\text{Te}_n$  would be formed and that in the presence of suitable organic compounds,  $\text{Na}_2\text{Se}_n$  or  $\text{Na}_2\text{Te}_n$  would react as fast as formed, and that the reaction would proceed until dyes would be formed. Many experiments were conducted at atmospheric pressure and in an autoclave, in which selenium or tellurium and sodium hydroxide or sodium carbonate were mixed with dinitrophenol, diphenylamine or *p*-phenylenediamine, and fused in a molten metal bath at temperatures ranging from 200° to 360°. The time of fusion varied from 6 to 48 hours, but no color was observed.

### Summary

1. Tellurium tetrabromide reacts with primary, secondary and tertiary organic bases to produce complexes.
2. Nine products were prepared and analyzed.
3. No selenium and tellurium dyes were prepared, analogous to the sulfur dyes, by substituting the element selenium or tellurium in place of sulfur.

PITTSBURGH, PENNSYLVANIA

[CONTRIBUTION FROM THE CHEMICAL RESEARCH LABORATORY OF FORDHAM UNIVERSITY]  
**SYNTHESIS OF AMINO ACIDS IN ANIMAL ORGANISMS. I.  
SYNTHESIS OF GLYCOCOLL AND GLUTAMINE IN THE HUMAN  
ORGANISM**

BY GEORGE J. SHIPLE AND CARL P. SHERWIN

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The fact that the human body is able to furnish glycocoll for the conjugation with benzoic acid has long been known and has been studied by many investigators.

Lewinski<sup>1</sup> observed neither benzoic acid nor benzoyl glucuronates in the urine of men to whom 12 to 20 g. of benzoic acid had been fed in small doses during the course of 12 hours. After feeding doses of 25 to 40 g., small amounts of benzoic acid (about 25% of the intake) were excreted as the free acid along with certain dextro-rotatory substances of a reducing nature indicating the presence of glucuronates. One may conclude from this that the average human adult is able to convert quantitatively about 20 g. of benzoic acid into hippuric acid. Brugsch<sup>2</sup> and Tsuschija,<sup>3</sup> on the contrary, were able to recover only about 25 to 50% of the ingested benzoic acid as hippuric acid. Dakin<sup>4</sup> found in his work with benzoic acid that doses of 5 to 10 g. of the acid ingested per day were almost entirely converted into hippuric acid before its elimination in the urine. The human body like that of the lower animals is therefore able to synthesize glycocoll within reasonable limits under conditions where no glycocoll occurs in the protein of the diet or even in a protein-free diet. Wiechowski<sup>5</sup> maintained that the glycocoll content of the tissues is insufficient to account for the quantity of glycocoll thus eliminated and that glycocoll can be synthesized at the expense of urea formed under normal conditions. Ringer<sup>6</sup> observed in his work an increase in the nitrogen elimination after feeding benzoic acid to animals and suggested that glycocoll resulted from the "extra destroyed protein" during this period. Epstein and Bookman,<sup>7</sup> experimenting on rabbits, concluded that benzoic acid as a toxic substance acts in a selective way causing the elimination of excessive amounts of nitrogen which is mostly excreted as hippuric acid nitrogen. McCollum and Hoagland<sup>8</sup> brought a pig of 46.7 kg. body weight into a condition of minimal nitrogen metabolism by feeding a diet of starch containing 75 calories for each kilogram of body weight. The diet was continued and increasing amounts of benzoic acid were fed. The results of their experiment show that when protein metabolism is reduced to a minimal level by carbohydrate ingestion the addition of benzoic acid does not affect the creatinine output, affects but little the total nitrogen, but may reduce the total elimination of urea nitrogen from 56% of the total nitrogen output to 19% of the total. This difference of 37% of the total nitrogen which is ordinarily converted into urea is under these circumstances eliminated as glycocoll.

Lewis<sup>9</sup> kept a man on a low protein diet containing no glycocoll for a period of 3

<sup>1</sup> Lewinski, *Arch. exp. Path. Pharm.*, **58**, 397 (1908).

<sup>2</sup> Brugsch, *Z. exper. Path. Therap.*, **5**, 731 (1909).

<sup>3</sup> Tsuschija, *ibid.*, **5**, 737 (1909).

<sup>4</sup> Dakin, *J. Biol. Chem.*, **8**, 103 (1909).

<sup>5</sup> Wiechowski, *Beitr. chem. Physiol.*, **7**, 204 (1906).

<sup>6</sup> Ringer, *J. Biol. Chem.*, **10**, 327 (1911).

<sup>7</sup> Epstein and Bookman, *ibid.*, **10**, 353 (1911).

<sup>8</sup> McCollum and Hoagland, *ibid.*, **16**, 299 (1913-1914).

<sup>9</sup> Lewis, *ibid.*, **18**, 225 (1914).

days. On the second day the subject ingested 8.47 g. of benzoic acid and the urine was collected at 2-hour intervals. Urea nitrogen and ammonia nitrogen were determined as one. During the first 2-hour period the amount of this nitrogen dropped from 80% to 67% of the total nitrogen; during the second 2-hour period, to 61.6%, and during the third to 64.9%, after which it returned to normal. This shows that the ingestion of 8.47 g. of benzoic acid may increase slightly the output of total nitrogen in the urine but at the same time cause a decided decrease in the amount of urea nitrogen plus ammonia nitrogen eliminated.

Thierfelder and Sherwin<sup>10</sup> have shown that glutamine is furnished by the human body for the detoxication of phenyl acetic acid and it was later found by Sherwin, M. Wolf and W. Wolf,<sup>11</sup> that 7.5 g. of glutamine was synthesized by the body on glutamine-(glutamic acid) free diet for the detoxication of ingested phenylacetic acid without materially increasing protein metabolism as shown by the total nitrogen and sulfur elimination.

In previous work a human subject had been reduced to a low protein diet<sup>9</sup> for a period of only 3 days and benzoic acid fed on only 1 day. It seemed to us important that the subject be reduced to an endogenous level of nitrogen metabolism, if possible, and the experiment be extended over a longer period. We also decided to feed first benzoic acid, then phenylacetic acid and lastly a mixture of the two in order to answer if possible the following questions: (1) What is the maximum amount of urea nitrogen which the human body will "side track" for the synthesis of glycocoll, and what influence if any has this on the other nitrogen constituents of the urine? (2) Can glutamine be synthesized at the expense of the urea nitrogen alone or does the amino and amide nitrogen necessary for this compound come from different sources? (3) Can glycocoll and glutamine be formed simultaneously in the human body, and if so which one is more readily formed when a limited supply of urea nitrogen is available?

The subject, a healthy man of 80 kg. body weight, was maintained on a diet of cream, bananas, and starch or lactose for a period of 7 days.

TABLE I  
INGESTED FOOD PER DAY, AND ITS ENERGY VALUE

Period	Starch	Lactose	Bananas	Cream	Total energy	Nitrogen in- gested in food
Days elapsed	G.	G.	G.	G.	Calories	G.
1	180	0	50	435	2475	0.080
2	50	120	325	100	1186	0.520
3	100	120	380	30	1314	0.610
4	100	110	420	10	1278	0.670
5	40	200	545	5	1581	0.870
6	40	200	335	0	1276	0.535
7	40	150	450	0	1197	0.720

<sup>10</sup> Thierfelder and Sherwin, *Ber.*, 47, 2630 (1914); *Z. physiol. Chem.*, 94, 1 (1915).

<sup>11</sup> Carl P. Sherwin, M. Wolf and W. Wolf, *J. Biol. Chem.*, 37, 113 (1918).

TABLE II—NITROGEN DATA

Period	Phenylacetic fed	Benzoic fed	Length of period	Urine Volume	Nitrogen					Percentage of total nitrogen					Amt. acid detoxicated			
	G.	G.	Hrs.	Cc.	Urea	Ammonia	Creatinine	Glycocoll	Glutamine	Urea	Ammonia	Creatinine	Glycocoll	Glutamine	Rest of Nitrogen	Benzoic	Benzoic fed	Phenylacetic
1	...	...	24	2100	15.88	12.3	0.62	1.15	0.53	77	7	4	...	...	12	...	...	Phenylacetic fed
2	...	...	24	2020	5.91	4.66	0.58	0.52	0.16	77	9	10	...	...	4	...	...	Phenylacetic
3	...	...	24	1000	5.71	4.23	0.56	0.45	0.15	74	8	10	...	...	8	...	...	G.
4	...	...	8	785	2.40	1.86	0.21	0.14	0.15	77	6	8	...	...	9	...	...	%
	...	3.0	6	685	1.95	0.93	0.15	0.18	0.15	48	9	8	17	...	18	2.8	93	%
	...	3.0	6	250	1.20	0.64	0.12	0.09	0.12	52	7	9	26	...	5	2.7	90	G.
	...	...	4	53	0.54	0.35	0.05	0.05	...	65	10	10	...	...	15	...	...	%
Totals	...	...	24	1773	6.09	3.78	0.53	0.46	0.63	60	8	9	10	...	13	5.5	92	G.
5	3.3	...	6	705	1.54	0.78	0.11	0.11	...	50	7	11	...	20	12	...	...	1.5
	...	...	6	415	1.77	0.69	0.14	0.15	...	35	39	8	...	20	24	...	...	1.7
	3.3	...	6	250	1.18	0.81	0.08	0.15	...	68	7	12	...	9	4	...	...	0.5
	...	...	6	135	0.96	0.34	0.10	0.15	...	35	10	16	...	31	8	...	...	1.4
Totals	...	...	24	1505	5.45	2.62	0.61	0.43	0.31	48	8	11	...	19	14	...	...	5.1
6	3.3	3.0	3	820	1.07	0.20	0.10	0.09	...	31	19	8	29	29	5	2.7	89	1.5
	...	...	3	286	0.83	0.38	0.12	0.06	...	45	8	14	...	24	9	...	...	1.0
	...	...	3	222	0.66	0.46	0.11	0.05	...	70	8	17	...	3	3	...	...	0.1
	...	...	15	675	2.22	1.68	0.27	0.21	...	76	9	12	...	...	3	...	...	...
Totals	...	...	24	2003	4.78	2.72	0.60	0.41	0.31	57	8	13	6	11	5	2.7	89	2.6
7	4.0	...	4	750	1.00	0.44	0.12	0.06	...	32	44	6	...	30	8	...	...	1.5
	...	...	4	555	1.31	0.32	0.11	0.14	...	24	11	8	...	38	18	...	...	2.4
	6.0	...	4	520	1.01	0.29	0.10	0.10	...	29	10	10	...	37	14	...	...	1.8
	...	...	4	255	0.97	0.12	0.09	0.10	...	12	10	9	...	52	16	...	...	2.5
	...	...	8	495	1.26	0.40	0.22	0.20	...	32	16	18	...	21	14	...	...	1.3
Totals	...	...	24	2575	5.55	1.57	0.64	0.60	...	28	11	12	...	21	14	...	...	9.5

The preceding table shows the weight of each substance eaten per day as well as its calorific value.

This diet which is practically nitrogen free insofar as utilizable nitrogen is concerned<sup>12</sup> is also of sufficient calorific value for the needs of a man undergoing only a small amount of physical exertion. Agar-agar was ingested in sufficient amounts to cause the regular evacuation of the intestine and thus avoid the absorption of nitrogenous end products of putrefaction.

In Table II, the days of acid feeding have been divided into sub-periods of varying length in order to study the amount of different substances excreted immediately after the ingestion of a given amount of acid. The acid ingested during a certain sub-period of the day was always taken at the beginning of that sub-period, and the entire output of urine collected during each sub-period was treated as a single unit. Also for each one of the last 4 days a sum total is given of all the sub-periods that the entire 24-hour period may be compared to one of the first 3 days of the control period.

A brief survey of Table II brings out clearly several interesting facts. Neither benzoic acid nor phenylacetic acid when fed in moderate doses (3 to 10 g.) to man acts as a stimulator of endogenous metabolism when the subject has been reduced practically to a state of endogenous protein catabolism. This is shown by the fact that the amount of total nitrogen excreted is not increased during the period of acid ingestion. It is also seen that neither glycocoll nor glutamine is built at the expense of "extra destroyed protein" but rather at the expense of one or more of the nitrogenous constituents of the urine, and of these only urea is affected to a marked degree.

Urea, during the control period, maintained an average of 74 to 77% of the total nitrogen, while during the feeding period it dropped to 60%, 57%, then to 48% and finally to 28% of the total nitrogen of the entire 24-hour period. If taken by sub-periods even more striking evidence is found of the inroads made on urea nitrogen for the purpose of glycocoll or glutamine synthesis. After a dose of 3 g. of benzoic acid on the fourth day, followed at the end of 6 hours by a second dose of 3 g. the urea nitrogen dropped to 48% and 52% respectively of the total nitrogen. On the fifth day 2 doses each of 3.3 g. of phenylacetic acid caused a further drop of the urea nitrogen to 39% and 35% respectively of the total nitrogen. It is interesting here to note that the effect of the benzoic acid on the urea nitrogen was immediate and largely confined to the sub-period at the beginning of which it was fed, while the greatest effect of the phenylacetic acid was seen in a later sub-period. One may infer from this that either the benzoic acid is more quickly absorbed than the phenyl-

<sup>12</sup> Lusk, "Science of Nutrition," W. B. Saunders and Co., 1919, p. 355.

acetic acid, or that glycocoll is more easily synthesized by the body than is glutamine. This latter inference one may explain on the ground that glutamine not only demands 2 atoms of nitrogen for its synthesis but besides an amine requires also an amide group.

During the seventh day of the experiment the greatest reduction is found in the urea nitrogen. At the beginning of the first 4-hour sub-period 4 g. of phenylacetic acid was ingested. This reduced the urea nitrogen to 44% of the total nitrogen, but caused a still greater fall in urea nitrogen (24% of total nitrogen) during the subsequent 4-hour sub-period. At this time a second dose of 6 g. of phenylacetic acid was ingested by the subject, but the percentage of urea nitrogen rose to 29%, only to fall 4 hours later to the very low value of 12% of the total nitrogen. This value was considerably lower than had been previously obtained. McCollum<sup>8</sup> found that the urea nitrogen fell to only about 20% of the total nitrogen after the feeding of large doses of benzoic acid to a pig, and that larger doses of the acid caused only an increase in protein metabolism and a subsequent increase in total nitrogen excreted. In this case, however, the entire 24 hours was considered as a unit. On the seventh day of our experiment it will be seen that the urea nitrogen for the entire 24 hours formed 28% of the total nitrogen.

The ammonia nitrogen was little, if at all, affected by the feeding of either of these organic acids. It has been previously shown by McCollum that an organic acid is detoxicated at the expense of the urea nitrogen, and an inorganic acid (hydrochloric acid) at the expense of the ammonia nitrogen.

It seemed probable that the amino nitrogen for glutamine synthesis would be taken from the urea fraction, but just possible that the ammonia nitrogen might be required to build the amide portion of the molecule. That this is not the case is shown by the fact that there is no decrease in ammonia nitrogen after the ingestion of 10 g. of phenylacetic acid on the last day of the experiment.

Creatinine was unaffected by the acid ingestion, for the creatinine value remained particularly constant during the last days of the experiment.

Lewinski<sup>1</sup> found that 10 to 20 g. of benzoic acid ingested by a man and quantitatively converted into hippuric acid may remove as much as 35% of the total nitrogen in the form of glycocoll (hippuric acid) nitrogen. Ringer<sup>6</sup> obtained much the same results with goats. Wiechowski,<sup>5</sup> employing guinea pigs, found that glycocoll nitrogen might run as high as 64% after the feeding of benzoic acid. After feeding the 6 g. of benzoic acid on the fourth day of our experiment 10% of the total nitrogen was found in the form of hippuric acid nitrogen. On the fifth day 19% of the total nitrogen appeared in the form of glutamine nitrogen. On the

sixth day after feeding 3.3 g. of phenylacetic together with 3 g. of benzoic acid, 6% of the total nitrogen appeared as glycocoll nitrogen and 11% as glutamine nitrogen. On the seventh day 35% of the total nitrogen was excreted in the form of glutamine nitrogen, which is comparable to figures found by some of the other investigators. Only in certain sub-periods of certain days does the excretion of glycocoll and glutamine nitrogen reach the value quoted by Wiechowski. In the first sub-period (3 hours) of the sixth day after the ingestion of 3.3 g. of phenylacetic acid and 3 g. of benzoic acid, 29% of the total nitrogen was found in the form of glycocoll nitrogen and 29% in the form of glutamine nitrogen, or a total of 58%. Again in the fourth sub-period (4 hours) of the seventh day after the ingestion of 10 g. of phenylacetic acid 52% of the entire nitrogen output of the sub-period appeared in the urine as glutamine nitrogen.

Moderate doses of benzoic acid are probably excreted quantitatively in the urine as hippuric acid. We found 89% to 93% so excreted within 6 hours after a 3g. dose. Phenylacetic acid seems to require about twice as much time as benzoic acid for its excretion (in the form of phenylacetyl glutamine). Its detoxication, moreover is apparently not so complete, for though after a dose of 10 g. we were able to recover 95% of it from the 24-hour sample of urine, still in other cases after small doses we recovered only about 78% of the amount fed.

Apparently the body builds both glutamine and glycocoll simultaneously as easily and efficiently as either of the compounds alone. After the ingestion of 3 g. of benzoic acid 92% of it was converted into hippuric acid within 6 hours. After the ingestion of 3.3 g. of phenylacetic acid on another day 44% of it was converted into phenylacetyl glutamine within 6 hours. When 3 g. of benzoic acid and 3.3 g. of phenylacetic acid were ingested simultaneously 89% of the benzoic acid and 46% of the phenylacetic acid were changed into their respective detoxication products within a period of 6 hours.

### Summary

It has been shown that man will synthesize glycocoll at the expense of urea as do the lower animals. The synthesis of another amino acid (glutamine) at the expense of urea nitrogen has also been demonstrated in the case of a man. The two amino acids may be built simultaneously as readily as either compound alone.

During the period in which these amino acids were being synthesized in the organism, urea nitrogen dropped from about 75% of the total nitrogen to 28%, and during a sub-period of a certain day, to the extremely low value of 12% of the total nitrogen.

After feeding a moderate dose of benzoic acid (3.3 g.), glycocoll for its



detoxication is built within 6 hours, while for the detoxication of a corresponding dose of phenylacetic acid a somewhat longer period of time is required for the synthesis of glutamine.

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## THE REACTION BETWEEN ALKALIES AND CERTAIN NITRO-CYCLOPROPANE DERIVATIVES

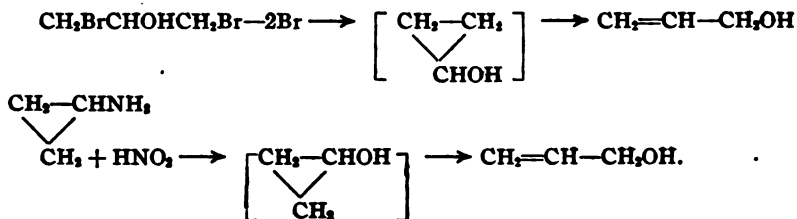
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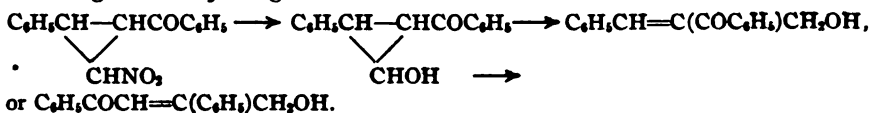
The action of alkalies on all known cyclopropane derivatives is peculiar. A typical reaction is that between phenyl-benzoyl-nitrocyclopropane and potassium hydroxide which gives potassium nitrite and an open chained  $\beta$ -diketone.<sup>1</sup>



Since the reaction involves the elimination of the nitro group, it is conceivable that the first step in the process might be the replacement of this group by hydroxyl. This would give as the primary product a cyclopropanol derivative; but it is probable that cyclopropanols are unstable and like the corresponding ethylenic compounds immediately undergo rearrangement, for when zinc removes bromine from dibromo-*isopropyl* alcohol the product is not the cyclopropanol which would be expected but allyl alcohol,<sup>2</sup> and when cyclopropyl amine is treated with nitrous acid the product is likewise the unsaturated and not the cyclic alcohol.<sup>3</sup>



A cyclopropanol obtained by replacing the nitro group with hydroxyl would therefore probably be unstable, but it would not be expected to rearrange into anything related to the diketone that is obtained:

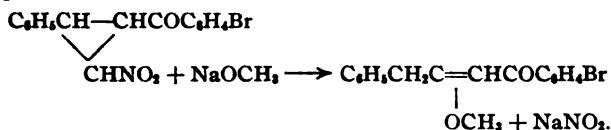


<sup>1</sup> THIS JOURNAL, 41, 1383 (1919).

<sup>2</sup> J. prakt. Chem., 46, 158 (1892).

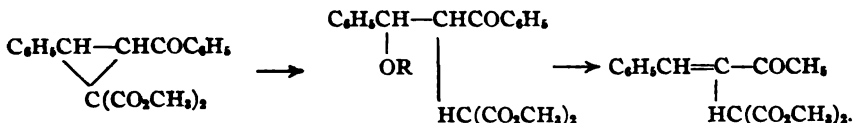
<sup>3</sup> Zentr., 76, [1] 1709 (1905).

Even if it were assumed that the benzoyl group in some way alters the mode of rearrangement it would still be impossible to account for the action of alcoholates upon the nitro compound. Cyclopropyl ethers ought to be at least as stable as cyclopropyl amines, but when these nitro compounds are treated with alcoholates they likewise yield only open chained compounds.<sup>4</sup>

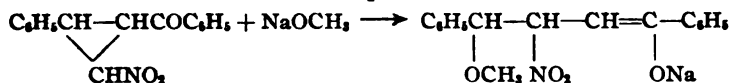


It seems certain, therefore, that the replacement of the nitro group is not the first step in the process.

Cyclopropane derivatives that are constituted like these nitro compounds but which have carboxyl in place of the nitro group are also exceedingly sensitive to alkalis. They behave like unsaturated compounds and it is always possible to account for the products obtained by assuming addition and subsequent elimination of water or alcohol.<sup>5</sup>



Meisenheimer<sup>6</sup> and Wieland<sup>7</sup> have shown that unsaturated as well as certain cyclic nitro compounds undergo remarkable transformations under the influence of alkalis. Like the reactions of the cyclopropane esters these generally start with the addition of alcoholates. It would not have been surprising, therefore, to find that these nitrocyclopropanes combine with alcoholates and thus form open chained compounds. It is quite certain, however, that if a compound which has both benzoyl and nitro groups were to combine with an alcoholate the metal would go to oxygen. In order to form the straight chain in both the diketone and the unsaturated methoxyl compound the ring must be opened between the phenyl and benzoyl groups. The addition of alcoholate would therefore have to take place as follows.



No plausible series of rearrangements of such an addition product could give the substances actually formed. The first step in the reaction is, therefore, not addition of the base.

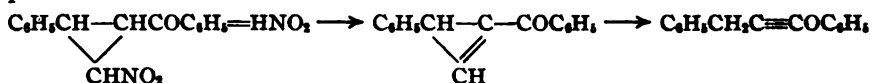
<sup>4</sup> THIS JOURNAL, 41, 1651 (1919).

<sup>5</sup> *Ibid.*, 39, 1408 (1917).

\* Meisenheimer, *Ann.*, 330, 145 (1904).

<sup>7</sup> Wieland, *ibid.*, 424, 102 (1921).

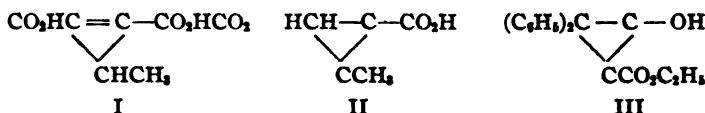
There remains the possibility that the first step in the process consists in the elimination of nitrous acid and that the resulting cyclopropene derivative immediately undergoes rearrangement to an acetylenic compound.



This mechanism would account admirably for the products that are obtained, because in the presence of alkalis acetylenic ketones readily combine with water to form  $\beta$ -diketones<sup>8</sup> and with alcohols to form unsaturated alkyloxy compounds.<sup>9</sup>

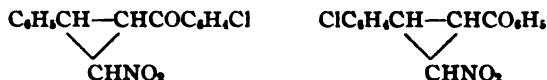
Nitrous acid is not one of the things that we commonly think of as being removed to form unsaturated compounds; but this may be due largely to our inadequate knowledge of aliphatic nitro compounds. In earlier papers<sup>10</sup> it was shown that some of these nitro compounds lose nitrous acid with great ease. The first assumption is, therefore, consistent with known facts.

There are few facts on which to base conclusions on the stability of cyclopropene derivatives. Only three such compounds have been described. By the action of alkalis on bromo-*isodehydro*-acetic ester Feist<sup>11</sup> obtained a dibasic acid which in all probability is the cyclopropene di-acid (I). Addition of bromine to this acid and subsequent reduction gave a new acid which Feist regards as an isomer of the first and to which he ascribes Formula II. Quite recently Staudinger<sup>12</sup> made a substance which he is inclined to represent by Formula III.



An examination of these formulas shows that none of these substances has the requisite number of hydrogen atoms to permit of rearrangement to an acetylenic compound. They therefore supply no useful evidence on the problem under consideration.

The following investigation was undertaken with a view to securing such evidence. Most of the experiments were performed with the two isomeric nitro cyclopropanes,



<sup>8</sup> Nef, *Ann.*, 308, 276 (1899).

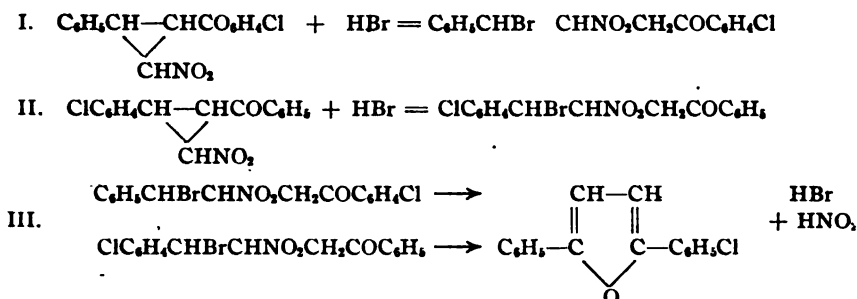
<sup>9</sup> Moureu and Brachin, *Ann. chim.*, 33, 131 (1905).

<sup>10</sup> THIS JOURNAL, 41, 1383, 1651, 1703 (1919).

<sup>11</sup> Feist, *Ber.*, 26, 750 (1893); 34, 136 (1911).

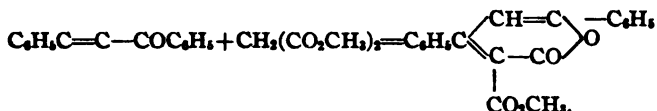
<sup>12</sup> Staudinger, *Helvetica Chim. Acta*, 4, 5 (1921).

These substances were easily made in accordance with the general scheme of adding nitromethane to unsaturated ketones, brominating the product, and eliminating hydrogen bromide from the resulting  $\alpha$ -bromo- $\gamma$ -nitro ketones. That they are isomeric cyclopropane derivatives is shown by the fact that they combine with hydrogen bromide to form isomeric addition products which lose nitrous and hydrobromic acids and yield the same furane derivative.



By loading the phenyl groups with chlorine atoms we hoped to diminish the solubility sufficiently to enable us to isolate intermediate cyclopropane derivatives. This was not realized; these compounds react less readily with alkalis than those described in earlier papers and the reactions are correspondingly more confused. We therefore turned our attention to the next stage, the acetylenic ketones. These likewise could not be isolated, but we secured very definite evidences of their presence in the alkaline liquids.

In a recent paper<sup>13</sup> it was shown that in the presence of alkalis malonic esters rapidly combine with acetylenic ketones and form sparingly soluble  $\alpha$ -pyrone derivatives which have very characteristic properties.



We have found, now, that similar pyrone esters are formed when nitrocyclopropane derivatives are treated with alkali in the presence of malonic ester. In order to get these pyrone esters it is necessary to add the malonic ester before the alkali; not a trace of the substances is obtained if the reagents are applied in the reverse order. This shows that they are formed from an intermediate compound which rapidly disappears in the alkaline medium. We regard this as a proof that acetylenic ketones play a part in the reaction and it seems almost equally certain that cyclopropane derivatives which have the requisite number of hydrogen atoms readily undergo rearrangement to isomeric acetylenic compounds.

<sup>13</sup> THIS JOURNAL, 44, 379 (1921).

The study of the action of alkalis on the nitro cyclopropanes has led to the discovery that alcoholic ammonia rapidly transforms these substances into isomeric compounds. These are stereo-isomers, for boiling alcoholic potassium acetate converts either isomer into a mixture of the two, and whenever both substances enter into the same reaction they give the same products. The isomers, however are remarkably different in activity. The lower-melting derivatives that are obtained by eliminating hydrogen bromide from bromo ketones are unsaturated compounds. They combine with hydrogen and with hydrogen bromide as readily and in the same manner as would the corresponding ethylenic ketones. The higher-melting isomers show none of this unsaturation. The activity of cyclopropane derivatives, therefore, depends to an extraordinary degree upon the space relations of the substituting groups.

### Experimental Part

$\beta$ -Phenyl- $\gamma$ -nitro- $p$ -chloro-butyrophenone,  $C_6H_5CHCH_2COC_6H_4Cl$ .—Sodium ni-



tromethane combines readily with benzal- $p$ -chloro-acetophenone when a thin paste of the sodium compound in dry methyl alcohol is added to a suspension of the ketone in the same solvent and the mixture is heated to the boiling point. The nitro ketone itself is obtained by acidifying the cold, clear, amber colored solution. This must be done with great caution, for, if the acid is added too rapidly, the precipitate is an oil from which it is almost impossible to obtain any solid ketone. The yield, about 70%, is better with small than with large quantities.

The ketone crystallizes from methyl alcohol in white needles that melt at 80°.

*Analysis.* Calc. for  $C_{16}H_{14}O_3NCl$ : C, 63.2; H, 4.6. Found: C, 63.8; H, 4.6.

$\beta$ -Phenyl- $\gamma$ -nitro- $\alpha$ -bromo- $p$ -chloro-butyrophenone,  $C_6H_5CHCHBrCOC_6H_4Cl$ .—



The bromination of the ketone was carried out in chloroform. The reaction is sluggish and unless the ketone is very pure it is best to start it with a drop of acetone. It results in a mixture of isomeric bromine compounds, only one of which was isolated in pure form. This crystallized in thin white needles and melted at 88–89°. An analysis of the washed and dried mixture showed that it was composed mainly of isomeric compounds.

*Analysis.* Calc. for  $C_{16}H_{13}O_3NClBr$ : C, 50.2; H, 3.4. Found: C, 49.4; H, 3.8.

1-[ $p$ -chloro-benzoyl]-2-phenyl-3-nitro cyclopropane,  $C_6H_5CHCHCOC_6H_4Cl$ .—The



cyclopropane ring was closed by eliminating hydrogen bromide from the bromo compound with potassium acetate in the usual manner. The yield from pure bromine compound is about 65%. It is not necessary, however, to use pure bromo ketone for making the cyclopropane derivative. Indeed, we seldom isolated any of the intermediates between the unsaturated ketone and the cyclopropane derivative. Generally our procedure was as follows. The crude nitro ketone that was precipitated on acidifying the condensation product was thoroughly washed with water and a little methyl alcohol, then immediately dissolved in chloroform. The chloroform solution was dried

with calcium chloride, warmed and treated with bromine in slight excess. Solvent and excess of bromine were then evaporated. The residue, a thick, orange colored oil, was dissolved in methyl alcohol and treated with potassium acetate in the usual manner.

The cyclopropane derivative was purified by crystallization from methyl alcohol; it separates in needles and melts at 121°.

*Analysis.* Calc. for  $C_{16}H_{15}O_2NCl$ : C, 63.7; H, 4.0. Found: C, 63.7; H, 4.5.

**ISOMERIC CYCLOPROPANE DERIVATIVE.**—The product obtained by the action of potassium acetate on the bromo ketone always melts at 120°, but it can be converted into an isomer by treatment with ammonia, weak bases, or even a boiling solution of potassium acetate. The most effective of these agents is ammonia. Ten g. of the finely powdered substance was suspended in 20 cc. of dry methyl alcohol which had been saturated with ammonia at 0°. The mixture was allowed to warm and stand in a stoppered flask overnight, when the solid was filtered and recrystallized from methyl alcohol. This gave 7.5 g. of a product that crystallized in flat needles and melted at 144°.

*Analysis.* Calc. for  $C_{16}H_{15}O_2NCl$ : C, 63.7; H, 4.0. Found: C, 63.9; H, 4.1.

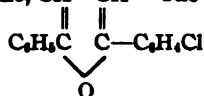
When the transformation is incomplete, either because less concentrated ammonia is employed or because the process is stopped too soon the product melts not quite sharply at 103–106°. The same product is obtained when the lower-melting cyclopropane derivative is digested with dilute alkalis or when either of the cyclopropane derivatives is boiled with a solution of potassium acetate. It ultimately proved to be a mixture which, owing to the solubility relations, it is extremely difficult to separate. It can, however, be separated by dissolving it in a large volume of boiling ethyl alcohol, carefully avoiding contamination while this solution is cooling and then inoculating it, first with the high-melting, and then with the low-melting component.

**$\beta$ -Nitro- $\gamma$ -bromo- $\gamma$ -phenyl- $p$ -chloro-butyrophenone,  $C_6H_5CHBrCHNO_2CH_2COC, H_4Cl$ .**—The low-melting cyclopropane derivative combines with hydrogen bromide very readily, while the high-melting one combines with it only with great difficulty, if at all. A solution of 2 g. of the lower-melting isomer in 25 cc. of glacial acetic was cooled to 0° and saturated with hydrogen bromide. The solution was cooled in a freezing mixture and allowed to stand for an hour during which a colorless solid separated in granular form. This was purified by dissolving it in a little cold chloroform and filtering the solution into twice its volume of methyl alcohol. It crystallizes in plates which turn green and begin to soften at about 105°, and melt with effervescence at about 128°.

*Analysis.* Calc. for  $C_{16}H_{15}O_2NClBr$ : C, 50.2; H, 3.4. Found: C, 49.8; H, 3.4.

When the higher-melting isomer was treated in the same way it was recovered unchanged even after the solution had stood overnight. After more protracted action at the ordinary temperature some of it had disappeared but the product was oily and it was impossible to determine the nature of the process that had taken place.

**1-Phenyl-4-( $p$ -chlorophenyl)-furan,  $CH=CH$ .**—The hydrogen bromide addition



product to the cyclopropane derivative loses both hydrobromic and nitric acids with the greatest ease, and passes into a furane derivative. This may be made by maintaining the bromo compound above the melting point until effervescence ceases; but it is easier to obtain it by boiling an alcoholic solution of the same compound for

several hours. The furane derivative separates from this solution in pale yellow flakes which melt at 123°.

*Analysis.* Calc. for  $C_{10}H_{11}OCl$ : C, 75.4; H, 4.4. Found: C, 75.6; H, 4.5.

**ACTION OF ALKALIES ON THE CYCLOPROPANE DERIVATIVE.**—The nitrocyclopropane derivative seems to be incapable of forming a metallic derivative. Cold conc. aqueous potassium hydroxide has no effect on it whatsoever. Dil. alcoholic potassium hydroxide and conc. alcoholic ammonia merely turn the lower into the higher melting isomer. This may take place through a metallic derivative but there is no evidence that such is the case. Cold conc. alcoholic potassium hydroxide and cold alcoholic sodium methylate attack both isomers, and the solutions turn slightly yellow in color; but nitrites begin to separate at once and it is impossible to secure any evidence that metallic derivatives are formed.

**Phenacetyl-*p*-chloro-acetophenone**,  $C_6H_5CH_2COCH_2COC_6H_4Cl$ .—This is the sole organic compound that could be isolated from the product of the action of conc. alkalies upon either of the isomeric nitrocyclopropanes. It is most easily obtained by treating the lower-melting isomer with sodium methylate. Ten g. of this substance was added to a solution of 10 g. of sodium in dry methyl alcohol, the mixture heated until the solution was clear, allowed to stand for an hour during which sodium nitrite separated, and then cooled in a freezing mixture and poured into iced hydrochloric acid. The resulting mixture was extracted with ether and the ethereal solution repeatedly shaken with small quantities of copper acetate solution. It gave about 4 g. of a light gray copper compound, which melted with decomposition at 218–220°.

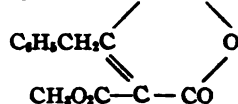
The copper compound was decomposed with dil. acid, and the resulting diketone recrystallized from methyl alcohol. It crystallized in plates and melted at 78°.

*Analysis.* Calc. for  $C_{18}H_{15}O_2Cl$ : C, 70.4; H, 4.8. Found: C, 70.5; H, 5.1.

The structure of the diketone was established by synthesis from ethyl phenylacetate and *p*-chloro-acetophenone, in accordance with the general procedure recommended by Bulow Grotowski.<sup>14</sup> This gave the same substance with a yield of about 40%.

With a view to stopping the reaction at an earlier stage the two nitrocyclopropanes were boiled with potassium acetate in methyl alcohol. This had no effect whatsoever on the higher melting substance and merely transformed the lower into the higher melting isomer.

**Methyl-3-benzyl-5-[*p*-chlorophenyl]-pyrone carboxylate-2**,  $CH=C-C_6H_4Cl$ .



—The pyrone ester was formed when either of the isomeric nitrocyclopropanes was warmed with a methyl alcoholic solution of the sodium derivative of dimethyl malonate. Thus 11 g. of the finely powdered cyclopropane derivative was added to a solution obtained by dissolving 1.6 g. of sodium and 9 g. of dimethyl malonate in 70 cc. of dry methyl alcohol. There was no evidence of action in the cold, but when the solution was warmed for a few minutes it suddenly turned blood-red in color, the temperature rose to the boiling point, and the solid cyclopropane derivative rapidly disappeared. A part of the product crystallized when the blood-red solution was cooled in a freezing mixture; the rest was precipitated by acidifying the solution with glacial acetic acid. The solid was purified by dissolving it in boiling chloroform and pouring this solution into twice its volume of boiling methyl alcohol.

<sup>14</sup> Grotowski, *Ber.*, 34, 1483 (1901).

*Analysis.* Calc. for  $C_{10}H_{11}O_4Cl$ : C, 67.7; H, 4.3. Found: C, 68.0; H, 4.4.

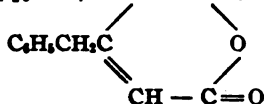
The pyrone derivative crystallizes in long colorless needles which have a beautiful sky-blue fluorescence and melt at  $171^\circ$ . It is very sparingly soluble in alcohol and in ether, moderately soluble in acetone, readily soluble in boiling chloroform and in benzene. The yield was small, about 20%. It was not increased either by varying the relative amounts of ester and alcoholate, or by changing the concentration of the alcoholic solution.

**THE PYRONE ACID.**—It was shown in a recent paper that  $\alpha$ -pyrone esters that have an ester group in the 3-position can be distinguished from their isomers by their behavior towards alkalis; they can be hydrolyzed to the corresponding acid. The pyrone in question is hydrolyzed with difficulty, but a fair yield of the acid was obtained by proceeding as follows. A solution of sodium methylate was prepared by dissolving 0.7 g. of sodium in 20 cc. of methyl alcohol to which 0.5 cc. of water had been added. This was dropped into a boiling solution of 3.5 g. of the ester in benzene. As long as any ester remained in the benzene layer each addition of alkali produced a blood-red color which rapidly faded to yellow. The mixture was poured into water and the stronger alkaline aqueous layer acidified with hydrochloric acid. This precipitated a mixture of solid and oily acids which was dissolved in ether, and ultimately separated into a yellow acid which melted with decomposition at  $155$ – $157^\circ$ , and a colorless acid which melts with effervescence at about  $147^\circ$ .

The yellow pyrone acid crystallizes from alcohol in thick prisms. It is sparingly soluble in ether, but readily soluble in alcohol.

*Analysis.* Calc. for  $C_{10}H_{11}O_4Cl$ : C, 67.0; H, 3.8. Found: C, 66.5; H, 3.8.

**4-Benzyl-6-[*p*-chlorophenyl]-pyrone,**  $CH=CC_6H_4Cl$ .—The pyrone acid



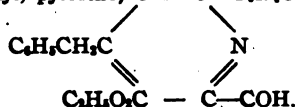
was heated in a metal bath to  $165$ – $170^\circ$  until evolution of gas ceased. The residue, which solidified on cooling, was recrystallized from methyl alcohol. It separated in pale yellow plates which melted at  $167$ – $168^\circ$ ; it did not reduce permanganate, and was insoluble in concentrated aqueous alkali.

*Analysis.* Calc. for  $C_{18}H_{17}O_4Cl$ : C, 72.8; H, 4.4. Found: C, 72.5; H, 4.6.

**$\beta$ -Benzyl- $\gamma$ -(*p*-chlorobenzoyl)-crotonic acid,**  $ClC_6H_4COCH_2C(CH=C_6H_5):CHCO_2H$ .—The colorless acid which is obtained as a by-product in the hydrolysis of the pyrone ester readily reduces permanganate. It is evidently an unsaturated acid formed by opening the pyrone ring. The double linkage was not located, but as the acid loses carbon dioxide at the melting point it is probably next to the carboxyl group as indicated.

*Analysis.* Calc. for  $C_{18}H_{17}O_5Cl$ : C, 68.7; H, 4.8. Found: C, 68.8; H, 4.8.

**1-Hydroxy-2-carboxyethyl-3-benzyl-5-(*p*-chlorophenyl)-pyridine,**  $CH=C-C_6H_4Cl$



A suspension of 5.6 g. of the pyrone ester in 50 cc. of a saturated solution of ammonia in dry methyl alcohol was shaken overnight. The liquid was then pale yellow in color and it held a small quantity of a fine powder in suspension. This was removed by filtration and the filtrate allowed to evaporate slowly in the air. It deposited a mass of fluffy needles which were recrystallized from a mixture of chloro-



form and methyl alcohol. The substance melted fairly sharply but on analysis it gave results that were persistently high, for both carbon and hydrogen. An examination of the alcohol obtained by hydrolyzing it showed that at some stage one of the substances had come in contact with ethyl alcohol and that the methoxyl group had been replaced by ethoxyl. The ester melts at 210°.

*Analysis.* Calc. for  $C_{11}H_{13}O_2NCl$ : C, 68.6; H, 4.91. Found: C, 68.4; H, 9.4.

$\beta$ -[*p*-Chlorophenyl]- $\gamma$ -nitrobutyrophenone,  $ClC_6H_4CHCH_2COC_6H_5$ .—An excellent

$$\begin{array}{c} | \\ CH_2NO_2 \end{array}$$

yield of this nitro ketone was obtained by condensing nitromethane with *p*-chlorobenzal-acetophenone in the usual way. It crystallizes from methyl alcohol in needles and melts at 96°.

*Analysis.* Calc. for  $C_{16}H_{14}O_2NCl$ : C, 63.2; H, 4.6. Found: C, 62.8; H, 4.2.

$\alpha$ -Bromo- $\beta$ -[*p*-chlorophenyl]- $\gamma$ -nitro-butyrophenone,  $ClC_6H_4CHCHBrCOC_6H_5$ .—

$$\begin{array}{c} | \\ CH_2NO_2 \end{array}$$

Bromination of the nitro ketone gave a mixture of two stereo-isomeric bromine derivatives. One of these, the principal product, was isolated in pure condition. It crystallized in white needles melting at 116°.

*Analysis.* Calc. for  $C_{16}H_{13}O_2NClBr$ : C, 50.2; H, 3.4. Found: C, 50.1; H, 3.4.

1-Benzoyl-2-[*p*-chlorophenyl]-3-nitrocyclopropane,  $ClC_6H_4CH\begin{array}{c} \diagup \\ \diagdown \end{array}CHCOC_6H_5$ .—The

$$\begin{array}{c} \diagup \\ \diagdown \end{array} \begin{array}{c} CHNO_2 \end{array}$$

yield of cyclopropane derivative obtained by eliminating hydrogen bromide from the bromo compound with potassium acetate was extremely poor, about 20%, but all efforts to improve it failed. The substance crystallizes with alcohol of crystallization. Immediately after removal from the solution it melts sharply at 59°, but on exposure to the air it soon becomes sticky. In this form it loses alcohol very slowly, but in the course of 2 or 3 weeks, during which it resolidifies, its weight becomes constant, and it then melts at 66–67°.

*Analysis.* Calc. for  $C_{16}H_{13}O_2NCl$ : C, 63.7. H, 4.0. Found: C, 63.1; H, 4.3.

ISOMERIZATION.—Like all the other nitrocyclopropane derivatives of this series, this one is very readily changed into a higher-melting less active stereoisomer. This is most conveniently accomplished by allowing the finely powdered solid to remain in contact with a saturated solution in alcohol. Under the most favorable conditions this gives a product which melts at 157–159°.

*Analyses.* Calc. for  $C_{16}H_{13}O_2NCl$ : C, 63.7; H, 4.0; N, 4.6. Found: C, 63.6; H, 4.1; N, 4.9.

Under less favorable conditions the action of ammonia gives a product that melts at 110–112°. This has the same composition as the former and is in all probability composed of mixed crystals similar to those described in an earlier part of this paper.

*Analyses.* Calc. for  $C_{16}H_{13}O_2NCl$ : C, 63.7; H, 4.0; Cl, 11.4. Found: C, 63.8; H, 4.1; Cl, 11.2.

$\beta$ -Nitro- $\gamma$ -bromo- $\gamma$ -(*p*-chlorophenyl)-butyrophenone,  $ClC_6H_4CHBrCHNO_2CH_2COC_6H_5$ .—Twenty g. of the cyclopropane derivatives melting at 67° was dissolved in 50 cc. of glacial acetic acid, and the solution was cooled, saturated with hydrogen bromide and allowed to stand. As no solid separated in the course of an hour, the mixture was poured into cracked ice and the oily precipitate extracted with ether. The dried ethereal solution on evaporation deposited 10 g. of a crystalline solid which, after recrystallization from ether-alcohol, melted with effervescence at 112–114°.

**Analysis.** Calc. for  $C_{16}H_{17}O_2NCIBr$ : C, 50.2; H, 3.4. Found: C, 49.8; H, 3.6. The high-melting cyclopropane derivative does not combine with hydrogen bromide; it was recovered unchanged even after the solution in glacial acetic acid was saturated with hydrogen bromide at zero and allowed to stand at the ordinary temperature overnight.

**$\beta$ -Nitro- $\gamma$ -hydroxy- $\gamma$ -(*p*-chlorophenyl)-butyrophenone**,  $ClC_6H_4CHOHCHNO_2CH_2COC_6H_5$ .—The hydrogen bromide addition product very easily loses both nitrous and hydrobromic acids and passes into the same furane that was described earlier in the paper. By very cautious treatment with silver acetate, however, it is possible to replace the bromine with hydroxyl. For this purpose an alcoholic solution of 5 g. of the addition product and 2.1 g. of silver acetate was gently warmed and persistently shaken for an hour. The silver bromide was then removed and the filtrate cooled in ice water. It deposited a crystalline solid which was purified from alcohol from which it separated in needles melting at  $142^\circ$ .

**Analysis.** Calc. for  $C_{16}H_{17}O_4NCI$ : C, 60.4; H, 4.4. Found: C, 60.5; H, 4.4.

The hydroxyl compound reduces permanganate. When treated with alkalis it loses water and nitrous acid and forms the same furane that is obtained by heating the bromine compound.

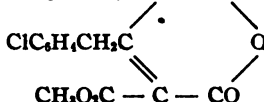
**$\alpha, \gamma$ -Dibromo- $\beta$ -nitro- $\gamma$ -(*p*-chlorophenyl)-butyrophenone**,  $ClC_6H_4CHBrCHNO_2CH_2BrCOC_6H_5$ .—The hydrobromic acid addition product is very easily brominated. The product crystallizes in plates and melts at  $143^\circ$ . The substance was made for the purpose of determining which of the two stereo-isomeric bromine compounds would be obtained when bromine was eliminated, but all attempts to remove the bromine and leave the rest of the molecule intact were unsuccessful.

**Analysis.** Calc. for  $C_{16}H_{15}O_2NCIBr_2$ : C, 41.6; H, 2.6. Found: C, 41.2; H, 2.7.

***p*-Chloro-phenacetyl-acetophenone**,  $ClC_6H_4CH_2COCH_2COC_6H_5$ .—The behavior of the nitrocyclopropane towards alkalis is exactly like that of the isomer described earlier in the paper. The product of the action of sodium methylate is a diketone which melts at  $52-54^\circ$  and forms a gray-green copper derivative that melts with decomposition at  $229-230^\circ$ .

**Analysis.** Calc. for  $C_{16}H_{15}O_3Cl$ : C, 70.4; H, 4.8. Found: C, 70.0; H, 4.8.

**Methyl-4-(*p*-chlorophenyl)-pyrone-carboxylate-3**,  $CH=C(C_6H_4)OCH_2CO_2CH_3$ .—Nine g. of the



finely powdered cyclopropane derivative was added in small portions to a solution of 1.4 g. of sodium and 9 g. of dimethyl malonate in 50 cc. of dry methyl alcohol. The nitro compound dissolved rapidly in the cold and the solution assumed the characteristic blood-red color. It was cooled in a freezing mixture and acidified with 4 g. of glacial acetic acid. The solid that separated was recrystallized from methyl alcohol which deposited it in long silky needles that showed the blue fluorescence characteristic of these pyrone esters.

**Analysis.** Calc. for  $C_{20}H_{19}O_4Cl$ : C, 67.7; H, 4.3. Found: C, 67.2; H, 4.6.

### Summary

1. The elimination of hydrogen bromide from  $\alpha$ -bromo- $\gamma$ -nitro ketones results in the formation of nitrocyclopropane derivatives which com-

bine with hydrogen bromide as readily as do ethylenic ketones, and the mode of addition is the same in both cases.

2. Ammonia transforms these substances into stereo-isomers which do not combine with hydrogen bromide

3. Although these cyclopropane derivatives are constituted like secondary nitro compounds they do not form metallic derivatives.

4. Concentrated alkalis remove nitrous acid from the nitrocyclopropanes and transform them into diketones. The probable steps in this process are: first, elimination of nitrous acid; second, rearrangement of the resulting cyclopropane to an acetylenic ketone; third, addition of water to the ketone.

CAMBRIDGE 38, MASSACHUSETTS

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE JOHNS HOPKINS UNIVERSITY]

## SESQUI-MUSTARD GAS OR BIS- $\beta$ -CHLORO-ETHYL ETHER OF ETHYLENE DITHIO-GLYCOL

BY RAPHAEL ROSEN AND E. EMMET REID

Received December 2, 1921

In view of the remarkable properties shown by  $\beta\beta'$ -dichloro-ethyl sulfide, it seemed of interest to prepare a compound of the same type but having 2 sulfur atoms separated by an ethylene group,  $\text{ClCH}_2\text{CH}_2\text{SCH}_2\text{CH}_2\text{SCH}_2\text{CH}_2\text{Cl}$ , with a view to comparing the chemical and physiological properties with those of the monosulfur compound.

Two ways of preparing the corresponding dihydroxy compound were studied; (1) the reaction of the sodium salt of monothio-glycol on ethylene bromide and (2) of ethylene chlorohydrin on the sodium salt of ethylene dithio-glycol.

**Preparation of Monothio-ethylene Glycol,  $\text{HSCH}_2\text{CH}_2\text{OH}$ .**—Our work with this compound was done before the paper of Bennett<sup>1</sup> came to hand, but our conclusions agree well with his, though our yields were not so good. We, too, had great difficulty in repeating the work of Carius.<sup>2</sup> In a number of experiments, in which his directions were followed as closely as possible, we obtained only insignificant yields.

The best method we found to be as follows.

Two hundred and forty g. of crystallized sodium sulfide is melted on the water-bath and saturated with hydrogen sulfide; 150 g. of alcohol is added and the mixture resaturated. To this solution, which is kept below  $20^\circ$ , 120 g. ethylene chlorohydrin is added slowly. This material is allowed to stand for 36 hours at room temperature. Then hydrogen chloride is passed in until the mixture is acid, and the sodium chloride filtered off. The filtrate is fractionated under reduced pressure. The yield was 26 to

<sup>1</sup> Bennett, *J. Chem. Soc.*, 120, 422 (1921).

<sup>2</sup> Carius, *Ann.*, 124, 257 (1862).

30% of the pure mercaptan boiling at 52° at 12 mm. The mercaptan is colorless, has a characteristic odor and is very soluble in water, in alcohol and in ether.

The residue from the distillation, after the removal of sodium chloride, is a sirupy liquid containing ethylene disulfide which is precipitated by the addition of water, and  $\beta\beta'$ -hydroxy-ethyl sulfide which was identified by being transformed into mustard gas by conc. hydrochloric acid.

The lead compound of the mercaptan is yellow and only slightly soluble in alcohol. The mercurous compound is a white crystalline solid, soluble in hot alcohol and melting at 108°.

In alkaline solution, it reacts like other mercaptans;<sup>3</sup> a sulfonic acid group in the  $\alpha$  position in anthraquinone is replaced to give compounds of the type  $C_{14}H_7O_2SCH_2CH_2OH$ . A number of these have been made in this Laboratory and will be reported later.<sup>4</sup>

Dithio-ethylene glycol was prepared by the method of Fasbender<sup>5</sup> as modified by Hoffman and Reid<sup>4</sup> in this Laboratory. The original method yields a product containing 74% of the mercaptan, but, by distilling the reaction mixture in a vacuum instead of with steam, the pure mercaptan is obtained. This mercaptan can be determined by the method of Kimball, Kramer and Reid,<sup>6</sup> provided the mixture stands overnight after the addition of the iodine and before titration.

**Bis- $\beta$ -hydroxy-ethyl Ether of Ethylene Dithio-glycol.**— $HOCH_2CH_2SCH_2CH_2SCH_2CH_2OH$ .—To a mixture of 15 g. of monothio-ethylene glycol and 18 g. of ethylene bromide, 8 g. of powdered sodium hydroxide was added in small portions and the mixture was refluxed for an hour. The reaction product was extracted repeatedly with boiling ether. A flaky white substance separated as the extract cooled. This was recrystallized from absolute alcohol. The compound is waxy and hygroscopic and melts at 114–711°. On account of its properties it is difficult to purify, which explains the high sulfur content found, *vis.*, 37.39% instead of the calculated value, 35.18%.

The same compound was obtained from dithio-ethylene glycol and ethylene chlorohydrin in a similar way.

Attempts to prepare this compound by the use of alcoholic potash instead of the powdered sodium hydroxide were fruitless; a white flaky substance, insoluble in all common solvents and unreactive with the usual reagents, was always obtained. It is probable that vinyl derivatives are formed at first and that these polymerize to give the insoluble substance.<sup>7</sup>

<sup>3</sup> Reid, Mackall and Miller, *THIS JOURNAL*, 43, 2104 (1921).

<sup>4</sup> Hoffman and Reid, unpublished work.

<sup>5</sup> Fasbender, *Ber.*, 20, 460 (1887).

<sup>6</sup> Kimball, Kramer and Reid, *THIS JOURNAL*, 43, 1199 (1921).

<sup>7</sup> After this article had been submitted, that of Bennett and Whincop (*J. Chem. Soc.*, 120, 1860 (1921)) came to hand. They prepared the same compound in alcohol solution and speak of a "quantitative yield." I have asked Mr. W. S. Hoffman of this laboratory to repeat their work to clear up the discrepancy. After several trials, he has been able to obtain the dihydroxy compound in alcohol solution by their method, but only in 20% yield, and melting, after two recrystallizations from ether, at 56° (B. and W. give 64°); sulfur, found, 36.00%, instead of calc., 35.18%. The high melting point reported above must have been due to contamination with one of the ethylene polysulfides, indicated by the high sulfur content. The melting points of

From the dihydroxy compound, the dichloride was prepared by boiling the former with several parts of conc. hydrochloric acid for an hour. The chloride separates as a yellow oil which solidifies as it cools. It was recrystallized from hot alcohol and melted at  $64^{\circ}$ .

Calc.: S, 29.26. Found: 29.87. Calc.: Cl, 32.36. Found: 30.99.

This shows that some of the hydroxy compound was present. It is readily hydrolyzed.

Similarly the bromide was obtained and melted at  $90-94^{\circ}$ .

Calc.: S, 20.81. Found: 21.42. Calc.: Br, 51.88. Found: 50.73.

By heating the dihydroxy compound with acetyl chloride a liquid was obtained which seemed to be the di-acetate.

### Physiological Effects

On account of the higher molecular weight, the volatility is less and the vapors would not be expected to show the activity of the monosulfide. When a tiny particle is placed on the human skin, a burn is produced, but its effect is considerably less than that of mustard gas.<sup>8</sup>

Conjunctivitis of the eyes and a rash over hands and face were suffered by the operator while working with it.

### Summary

An analog of mustard gas,  $(\text{ClCH}_2\text{CH}_2\text{SCH}_3)_2$ , m. p.  $64^{\circ}$ , has been prepared and found to have decided vesicant action. The corresponding dihydroxy compound, m. p.  $114-117^{\circ}$ , was made as an intermediate.

BALTIMORE, MARYLAND

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF AMHERST COLLEGE]

## TRIHALOGEN-METHYL REACTIONS. IV. REACTION OF TRI-CHLORO-ACETIC ACID WITH COPPER

By HOWARD WATERS DOUGHTY AND BENJAMIN FREEMAN

Received December 12, 1921

For several years the senior author has been interested in the behavior of compounds which contain the trichloro- or tribromo-methyl group, with copper in presence of aqueous ammonia.<sup>1,2,3</sup> With the exception of benzotrichloride, all of this class of compounds which have been tested react with copper more or less rapidly in the presence of aqueous ammonia, all our samples were indefinite. Mr. Hoffman, by the use of thionyl chloride, has obtained the crude dichloride melting at  $53^{\circ}$  agreeing well with Bennett and Whincop who give  $54^{\circ}$  as the melting point of the unrecrystallized chloride.—E. E. R.

<sup>8</sup> Our thanks for the physiological tests are due to Lt. Harry A. Kuhn, Chief of the Dept. of Toxicology, Edgewood Arsenal.

<sup>1</sup> Doughty, *THIS JOURNAL*, **39**, 2685 (1917).

<sup>2</sup> Doughty, *ibid.*, **41**, 1129 (1919).

<sup>3</sup> Doughty and Freeman, *ibid.*, **43**, 700 (1921).

the copper passing into solution as ammonio-cupric chloride, while mono- or dihalogen methyl compounds react much less readily or not at all in similar environment, except ammonium dichloro-acetate, which does also react.<sup>4</sup> Ammonium trichloro-acetate is particularly noticeable for the violence of its reaction, and the present writers therefore decided to investigate the behavior of trichloro-acetic acid and its derivatives with copper, intending to conduct a similar investigation of the behavior of other substances which contain the trihalogen-methyl group, in the hope of finding some relation between the intensity of reaction and the "negativity" of the fourth substituent of the methane molecule in compounds of the general formula  $RCX_3$ , where R is a radical or hydrogen, and X a halogen atom. As the present writers are no longer in a position to carry on the work together, it is deemed advisable to make a statement of what has been accomplished by them so far.

Berthelot<sup>5</sup> prepared acetylene by passing chloroform vapor over heated copper. Cazeneuve,<sup>6</sup> in 1891, found that bromoform and iodoform react much more energetically with copper and that bromoform, gently warmed with silver powder, gives acetylene and the silver becomes incandescent, while iodoform reacts still more vigorously. On the other hand, chloroform, according to Cazeneuve, does not react at all with silver.

Beilstein<sup>7</sup> states that benzotrichloride, warmed with copper powder, reacts vigorously, forming first toluene tetrachloride and then toluene dichloride. He does not mention any evidence of the formation of toluene. Evidently the replacement of the hydrogen of chloroform by the phenyl group makes a considerable difference in the course of the reaction, though in both cases the tendency is towards the formation of acetylene derivatives. The problem for us in the present investigation is the determination of the effect of substituting a carboxyl group, instead of a phenyl group, for the hydrogen of chloroform.

### Some Derivatives of Tetrachloro-succinic Acid

Analogy to the action of chloroform and of benzotrichloride would suggest that the action of trichloro-acetic acid on copper might result in the formation of acetylene dicarboxylic acid or tetrachloro-succinic acid. The latter possibility is of particular interest from the fact that no mention

<sup>4</sup> Thanks to the courtesy of Professor Treat B. Johnson, of Yale University, and Mr. G. W. Pucher, we have obtained a considerable quantity of dichloro-acetic acid, prepared by the latter (*THIS JOURNAL*, 42, 2251 (1920)). We find that this acid, probably as pure as has ever been prepared, does react with copper and aqueous ammonia, and also with cuprous chloride in aqueous ammoniacal solution.

<sup>5</sup> Berthelot, *Compt. rend.*, 50, 805 (1860).

<sup>6</sup> Cazeneuve, *ibid.*, 113, 1054 (1891).

<sup>7</sup> Beilstein, "Handbuch der organischen Chemie," Leopold Voss, 3rd Ed., vol. II, p. 48.

of tetrachloro-succinic acid, its salts or its esters, is to be found in the literature, excepting "perchloro-succinic ester,"  $C_2Cl_4O_4$ , which is formed by the action of chlorine on diethyl succinate in the sunlight. This substance reacts with ammonia gas or liquid ammonia to form a substance which Malaguti<sup>8</sup> formulated as  $C_2HCl_3NO$ , and called chloro-azo-succinic acid while Laurent<sup>9</sup> considered it to be tetrachloro-succinimide,  $C_2Cl_4O_2NH$ . Anschütz and Beavis<sup>10</sup> prepared what they considered to be tetrachloro-succinanil, m. p.  $157^\circ$ , by the action of phosphorus pentachloride on the anil of dichloro-maleic acid. They do not offer any evidence for the formula assigned, other than analysis and the method of preparation. The other chloro-succinic acids have been prepared. The trichloro-succinic acid prepared by Van der Riet<sup>11</sup> is particularly significant as indicating the reason for the non-appearance of tetrachloro-succinic acid in the literature. He found that a mixture of chloro-maleic acid, water, and liquid chlorine in a sealed tube in the sunlight, gave an acid, soluble in ether, very hygroscopic, and hence not obtainable in pure condition. From this he prepared salts of various metals, all soluble in water excepting those of lead and silver, and also the aniline salt, m. p.  $146^\circ$  (with decomp.), which separates as a white crystalline precipitate when aniline is added to an alcoholic solution of the acid, and which is easily purified by recrystallization from alcohol. Analyses of these salts showed the acid to be trichloro-succinic acid.

The reaction of trichloro-acetic acid with copper powder is very vigorous and our first attempts to obtain a product of the reaction were not successful. We therefore turned our attention to the action of the ester, ethyl trichloro-acetate, on copper, thus introducing the carbethoxy group as R in the general formula,  $RCCl_3$ . The ester was prepared by saturating an alcoholic solution of pure trichloro-acetic acid with hydrogen chloride in the usual way. It boiled at  $165-167^\circ$ . In the following experiments copper was used in various forms. Copper powder was prepared by reduction of copper sulfate with zinc, with subsequent washing and drying. We also tried copper powder prepared by reducing copper oxide with hydrogen. The most effective form was found to be the "dark copper bronze" prepared for use with bronzing lacquers and obtainable from dealers in painters' and decorators' supplies.

**Diethyl Tetrachloro-succinate.**—Ethyl trichloro-acetate was heated on a water-bath and copper powder was added in 5g. portions, with stirring, at 10-minute intervals until about 3 moles of copper had been added to 2 moles of ester. The heating was continued for 6 to 8 hours. The liquid was then filtered off and the residue extracted with ether. The ether extract was added to the main filtrate, and the whole product

<sup>8</sup> Malaguti, Gerhardt, "Traité chim. organ.," vol II, pp. 466, 477.

<sup>9</sup> Laurent, *Compt. rend.*, 35, 381 (1852).

<sup>10</sup> Anschütz and Beavis, *Ann.*, 295, 33, 39 (1897).

<sup>11</sup> Van der Riet, *ibid.*, 280, 221, 230 (1894).

was fractionated under diminished pressure. A colorless, mobile liquid was obtained, having a pleasant, rather spicy odor, distilling at  $156^{\circ}$  (13 mm.). When heated to  $175^{\circ}$  under atmospheric pressure it decomposed, giving hydrogen chloride and a brown viscous residue.

*Analyses.* Calc. for  $C_4H_5O_4Cl_3$ : Cl, 45.54. Found: (Carius) 44.56, 44.58. Mol. wt. Calc.: 312. Found: 293.4. Saponification equivalent (g. of NaOH per g. of ester). Calc.: 0.2564. Found: 0.2676, 0.2504.

These analyses, while not indicating a high degree of purity of product, do show that the ester is in all probability diethyl tetrachloro-succinate. To test this further, the ester was reduced by heating with conc. hydriodic acid for several days in a flask with return condenser. The iodine which separated was filtered off, the solution decolorized by hydrogen sulfide and evaporated to dryness. From 13 g. of ester about 1 g. of an acid was obtained, light brown in color, which melted at  $180-181^{\circ}$ . With the same thermometer succinic acid melted at  $182^{\circ}$  and a mixture of the two in equal parts melted at  $181^{\circ}$ , proving conclusively that the product of reduction of the ester, with accompanying hydrolysis, is succinic acid, from which it appears highly probable that the ester is diethyl tetrachloro-succinate.

Attempts to saponify the ester by boiling with conc. hydrochloric acid were not successful. A dark colored tarry product was obtained from which no definite substance could be isolated.

**Aniline Tetrachloro-succinate.**—When trichloro-acetic acid and copper powder were intimately mixed the mixture became very hot, and a considerable part of the acid was lost by volatilization. By adding the copper in small portions and waiting for the reaction to subside, the temperature was kept below the boiling point of trichloro-acetic acid. The copper was added until 3 atoms of copper were present to 2 moles of trichloro-acetic acid. After cooling, the mixture was extracted with ether. The ether filtrate was evaporated, leaving a green sirupy mass. This was dissolved in alcohol and the copper precipitated by hydrogen sulfide. After filtering, the hydrogen sulfide was removed by partial evaporation under diminished pressure. The remaining solution, dark red in color, contained a strong acid. Aniline was added to this solution, which was then placed in the ice chest. After some hours a small quantity of small, fine, hard, white crystals formed, which melted at  $149-150^{\circ}$  (corr.). Analysis indicates that this substance is aniline tetrachloro-succinate.

*Analyses.* Calc. for  $C_4Cl_4H_2O_4 \cdot 2C_6H_5NH_2$ : Cl, 32.12; N, 6.33. Found: Cl (Carius) 32.32, 31.91, 32.29; N (Kjeldahl), 6.22. Subs. (aniline salt), 1.1711: 104.89 cc. of 0.1 N  $BaO_3H_2$  (thymol blue (blue-yellow)). Calc.: 105.94 cc.

Aniline tetrachloro-succinate is soluble in benzene, rather difficultly soluble in water, slightly soluble in ether, very slightly soluble in cold alcohol, but readily on heating. Boiled, or allowed to stand with water, it hydrolyzes easily, giving hydrochloric acid. The analyses might equally well indicate aniline dichloro-acetate, but this salt melts at  $122-123^{\circ}$ .

Although tetrachloro-succinic acid undoubtedly exists in the alcoholic solution mentioned above, after saturation with hydrogen sulfide, we have not been able to obtain the free acid in anything approaching pure condition. Apparently it resembles trichloro-succinic acid in being exceedingly hygroscopic, and it is also easily hydrolyzed and probably decomposes easily, to judge from the fact that the ester gives large amounts of hydrogen chloride when heated above  $175^{\circ}$ . The yield of aniline tetrachloro-succinate is small, never exceeding 5% of the weight of the trichloro-



acetic acid used in our experiments. Many attempts were made to increase the yield, by using various solvents to diminish the intensity of the reaction and by varying the conditions as to temperature and mixing, but we have not been able to obtain any considerable amounts of this salt. When water or benzene was used to dissolve the trichloro-acetic acid before adding the copper, no trace of aniline tetrachloro-succinate could be obtained.<sup>12</sup> It was obtained when the reaction took place in ether solution, but the yield was not very different from that obtained by the method described above, and in some experiments none was obtained.

### Preparation of Dichloro-Acetic Acid

The small yield of a salt of tetrachloro-succinic acid led to further study of the products of the reaction between trichloro-acetic acid and copper, particularly in aqueous and in benzene solution, from which it appears that only a relatively small part of the product is tetrachloro-succinic acid, and the principal product is dichloro-acetic acid. Indeed it appears that this reaction affords a very satisfactory means of preparation of the latter acid, either in aqueous solution or in the anhydrous condition.

Trichloro-acetic acid, 15 g., was dissolved in 100 cc. of benzene, and 15 g. of copper powder was added in 5g. portions at intervals of about 15 minutes. The mixture, which soon became warm, was stirred continuously with an electric stirrer for 2 hours. Hydrogen chloride was then passed into the mixture to convert any organic copper salts into cuprous or cupric chlorides, both of which are insoluble in benzene. After filtering from the copper chlorides, the hydrogen chloride was removed by partial evaporation in a vacuum.<sup>13</sup> When 9 g. of aniline was added to the remaining solution, about 12 g. of white crystalline precipitate was obtained, which proved to be aniline dichloro-acetate, m. p. 122–123°. In order to establish the identity of this product, aniline dichloro-acetate was also prepared from Pucher's dichloro-acetic acid<sup>14</sup> which had been subjected to further fractionation. The melting point of the aniline salt thus prepared was identical with that prepared as described from trichloro-acetic acid, and a mixture of the two products melted at the same temperature, 122–123°.

When water was substituted for benzene in the experiment just described, similar results were obtained. In this case, using 15 g. of trichloro-acetic acid and 10 g. of copper powder in 100 cc. of water, the green color appeared in 5 minutes, and in 30 minutes the temperature rose from 23° to 40°. After stirring for 1 hour the solution was filtered from unchanged copper and insoluble copper salts, and evaporated to dryness. The residue was pulverized, suspended in benzene, saturated with hydrogen

<sup>12</sup> In the abstract of the preliminary report of this work, which was presented at the Spring meeting of the American Chemical Society, 1921, and appeared in *Science*, (54, 35 (1921)) it was stated that good results were obtained by carrying out the reaction in benzene solution. The discrepancy in statement is due to the fact that the melting point of aniline trichloro-acetate is 147°, and therefore this salt, which is present if the reaction is incomplete, may be easily mistaken for aniline tetrachloro-succinate, m. p. 149–150°; it was so mistaken in some of the earlier experiments when the latter salt had not been obtained entirely pure and therefore melted slightly low.

<sup>13</sup> This precaution was probably unnecessary. Simply boiling the solution would doubtless have answered as well.

<sup>14</sup> Pucher, *THIS JOURNAL*, 42, 2251 (1920).

chloride, filtered from copper chloride, freed from hydrogen chloride by partial evaporation under diminished pressure and aniline was added. The yield of aniline dichloroacetate was 14.4 g.

While no attempt was made to determine the maximum yield of dichloroacetic acid by this method, it is evident that it is present in the benzene solution before addition of aniline, and could therefore be obtained very easily by fractional distillation. The method has obvious advantages over the older method<sup>15</sup> of preparation from chloral and potassium or sodium cyanide with the attending unpleasant evolution of large quantities of hydrocyanic acid.

In the preparation of dichloroacetic acid from trichloroacetic acid as described above, hydrogen sulfide can be used instead of hydrogen chloride to remove copper, but we have found hydrogen chloride to be the more satisfactory reagent. This method of preparation of dichloroacetic acid is now under investigation in this laboratory to determine the best conditions for obtaining a maximum yield. The results will be published shortly.

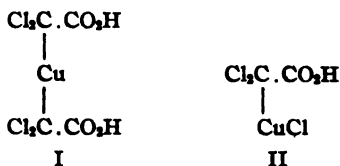
Dichloroacetic acid is also formed when trichloroacetic acid reacts with copper without any solvent. Copper dichloroacetate is found, together with cuprous chloride, in the residue after extraction with ether, and dichloroacetic acid is obtained by suspending this residue in benzene and treating with hydrogen chloride as described above. While we have no numerical data as regards the yield of dichloroacetic acid by this modification, it is apparently not so good as when a solvent is used.

**The Mechanism of the Reaction.**—The formation of dichloroacetic acid from trichloroacetic acid and copper involves the shifting of a hydrogen atom from its labile or ionizable position in the carboxyl group to a position of great stability when joined to the methane carbon atom as in dichloroacetic acid, which raises an interesting question as to the mechanism by which this change takes place. In fairly recent years copper has been used extensively as a condensing agent, particularly by Ullmann.<sup>16</sup> In some cases the action is apparently simply the removal of halogen atoms as in the Würtz or Fittig reaction; thus, with copper powder, iodobenzene gives diphenyl at 230°, and bromobenzene with ethyl chloroacetate gives ethyl phenylacetate at 180–200°. In other cases the action of copper powder appears to be catalytic, as in the reaction of *o*-chlorobenzoic acid with glyocoll to form phenylglycine-*o*-carboxylic acid, which is greatly accelerated by the addition of a very minute amount of copper powder. The results obtained in the present investigation appear to us to be somewhat suggestive in this connection.

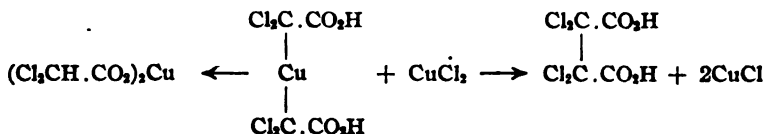
<sup>15</sup> Wallach, *Ann.*, 173, 288 (1874). Pucher, Ref. 14.

<sup>16</sup> Ullman, *Ber.*, 34, 2174, 3802 (1901); 36, 2383 (1903); 37, 853 (1904); 38, 729, 2120 (1905); 39, 1691, 2211 (1906); *Ann.*, 332, 38 (1904); 350, 83 (1906). See J. B. Cohen, "Organic Chemistry," Edward Arnold, Part I, p. 199.

When trichloro-acetic acid acted on copper in benzene solution a perfectly clear, dark green solution was obtained after filtering from the insoluble copper salts. After a short time a dark green amorphous precipitate separated from the benzene solution. After filtering again, a dark green, perfectly clear solution was again obtained, from which the dark green amorphous solid soon began to separate. This dark green solid substance, although separating slowly from a clear benzene solution, proved to be totally insoluble in benzene after it had once precipitated. When water was used as solvent in the preparation of dichloro-acetic acid, the copper salt obtained after evaporation of the aqueous solution was also insoluble in benzene. Copper dichloro-acetate, prepared from copper oxide and pure dichloro-acetic acid, is also almost quantitatively insoluble in benzene. It appears, therefore, that the compound which gives the dark green color to the benzene solution cannot be copper dichloro-acetate, nor can it be a chloride of copper, for both cupric and cuprous chlorides are insoluble in benzene. It seems to us that these observations may be satisfactorily explained as follows. Probably the reaction between copper and trichloro-acetic acid involves the formation of a rather unstable compound having the composition of Formula I



which is easily soluble in benzene, giving a dark green solution. Cupric chloride and probably cuprous chloride are formed at the same time. The organo-metallic compound may then react in two ways,



or possibly the initial condensation may give a compound similar to Formula II, two molecules of which may then eliminate cuprous chloride to form tetrachloro-succinic acid, or cupric chloride to form copper dichloro-acetate. There is at present no evidence which would enable one to choose between these possibilities. On either supposition, the relative amounts of tetrachloro-succinic acid and copper dichloro-acetate formed would depend upon the relative velocities of the respective reactions, which would doubtless be greatly affected by temperature and nature of solvent. While the evidence at present available is not sufficient to warrant more than a suggestion, it does seem to us that there is

here some indication as to the possible explanation of the mechanism of reactions in which copper powder or cuprous chloride is used as a condensing agent, not only those of the type mentioned above, but also such as the Sandmeyer and Gattermann reactions in which cuprous salts and copper powder, respectively, are used with diazonium salts. The analogy to the latter reactions is strengthened by the fact that trichloro-methyl compounds also react with cuprous chloride in presence of aqueous ammonia.<sup>2</sup>

So far as we are aware, no compound of the kind suggested has ever been described. Cupric and cuprous acetylides are indeed examples of copper directly linked to carbon, and their instability suggests that this linkage is generally unstable and that compounds of this type may be expected to undergo decomposition or rearrangement very readily to form more stable compounds. It is to be expected, however, that the stability of the copper-carbon linkage would be greatly affected by the nature of the other atoms or groups which are joined to the carbon atom to which the copper atom is also joined. Thus it should not be surprising that a carbon atom may be joined to negative atoms or groups in such a manner as to make the combination sufficiently negative to form a more or less stable linkage with copper, although such combination would be too unstable in most cases to permit isolation and purification of the compound. The relative ionization constants of the chlorinated acetic acids and of the unsaturated acids, such as acetylene dicarboxylic, acrylic, maleic and fumaric, furnish indication that it is precisely among highly chlorinated and unsaturated compounds that we should look for cases of relatively stable linkage between copper and carbon. The acetylides are examples of copper joined to carbon which is joined by the triple linkage to another carbon atom, and the formation of copper acetylides is limited to compounds containing the  $R-C\equiv C-H$  grouping, where copper may replace the hydrogen which is joined to a triply linked carbon. The very great strength of acetylene-dicarboxylic acid, as compared with succinic and maleic acids shows the great negativity of the acetylene linkage. If there is really any truth in the explanation which we offer of the reaction of copper with trichloro-acetic acid, there should be a possibility of similar, and probably more stable compounds of copper with carbon when the carbon atoms are contained in a more "negative" grouping than that represented by "trichloro-ethanoic acid." The replacement of the carboxyl group of this acid by chlorine, or the introduction of an unsaturated linkage in place of the carboxyl group and a chlorine atom would be in the nature of such increase of negativity, and it is precisely in such cases that we have observed the formation of compounds, as yet not further investigated, which appear to support our assumption.

When carbon tetrachloride reacts with copper in presence of aqueous

ammonia, one of the reaction products is a dark brown precipitate, insoluble in water, aqueous ammonia, or the ordinary organic solvents. This substance was washed free from chlorides, suspended in aqueous ammonia through which air was aspirated for 12 hours to remove free copper, and then washed free of ammonia and dried at room temperature. As thus obtained, the dark brown powder dissolved readily in hydrochloric acid, forming a dark maroon solution, which became somewhat lighter in color on addition of an excess of ammonia, but showed no trace of blue, indicating absence of copper ions. When the dark brown powder was heated in a dry tube, however, water was given off and a black residue remained which dissolved readily in hydrochloric acid and gave abundant tests for copper. The substance also apparently contains nitrogen.

In a previous communication<sup>17</sup> a color test for tetrachloro-ethylene was proposed, based upon the behavior of this substance with copper in the presence of aqueous ammonia. It was shown at that time that of all substances tested which contain the trichloro- or tribromo-methyl group, only one, benzotrichloride, failed to bring about fairly rapid solution of the copper to form the characteristic dark blue ammono-cupric solution. On the other hand, substances which did not contain this trihalogen-methyl group did fail to bring about solution of the copper, with two notable exceptions, namely, dichloro-acetic acid and tetrachloro-ethylene. The former contains, to be sure, only two chlorine atoms joined to the methane carbon atom, but there is in addition the negative carboxyl group, so that dichloro-acetic acid would be expected to behave in this respect somewhat similarly to chloroform, and it does. Tetrachloro-ethylene contains a double linkage and two chlorine atoms, joined to the methane carbon and, on the basis outlined above, would be expected to behave somewhat similarly to carbon tetrachloride in respect to its reaction with copper, and the experimental verification is striking. When tetrachloro-ethylene and copper are brought together in presence of aqueous ammonia there is evident and fairly rapid action, but no blue color appears. Instead, copper does go into solution slowly forming a dark maroon solution and, gradually, a dark brown precipitate. After long standing (the bottle was set aside for more than a year) the solution does show the dark blue color characteristic of the ammono-cupric ion. It seems probable that in this case there is the formation at first of a fairly stable organo-copper compound from which the copper is not ionized, which subsequently hydrolyzes or rearranges to give a substance which does give cupric ions. These supposed organo-copper compounds will be investigated as soon as circumstances permit.

The reaction of ammonium trichloro-acetate with copper in aqueous ammonia has not so far yielded satisfactory results. We have obtained

<sup>17</sup> Ref. 1, p. 2890.

a small amount of dichloro-acetic acid, separated and identified as its aniline salt, showing that the course of the reaction is probably similar to that when ammonia is not present, but it is evident that the reaction is more complicated, probably by reason of secondary reactions in which ammonia takes part.

### Summary

The reactions of trichloro-acetic acid and of ethyl trichloro-acetate with copper have been studied. Diethyl tetrachloro-succinate has been prepared by the action of copper with ethyl trichloro-acetate. It boils at 156° and 13 mm. pressure. Tetrachloro-succinic acid is formed in small amount by the action of copper with trichloro-acetic acid alone or in ether solution. The acid was not obtained in pure condition. Aniline tetrachloro-succinate was obtained, m. p. 149–150°.

Dichloro-acetic acid is formed in satisfactory quantity when trichloro-acetic acid reacts with copper powder in benzene or aqueous solution, and this reaction is recommended as a means of preparation of dichloro-acetic acid in any desired quantity.

Evidence is presented from which it seems probable that these reactions involve the formation of an intermediate relatively unstable compound in which copper is joined directly to carbon, and that the course of the reaction is determined by the manner in which the copper is eliminated from this intermediate compound. The suggestion is made that the action of copper as a condensing agent, as used by Ullmann, Sandmeyer and Gattermann, may involve the formation of similar intermediate compounds.

AMHERST, MASSACHUSETTS

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[CONTRIBUTION FROM THE LABORATORY OF PHARMACEUTICAL CHEMISTRY, UNIVERSITY OF WASHINGTON]

## THE ACTION OF NITROSYL CHLORIDE ON NORMAL HEPTANE

By E. V. LYNN AND O. HILTON

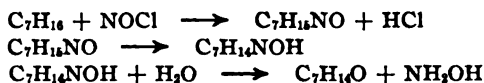
Received December 15, 1921

It has recently been found by one of us<sup>1</sup> that nitrosyl chloride will readily react with normal heptane in the sunlight, a reaction which is apparently general for the paraffin hydrocarbons. From a preliminary study of the products it was assumed that dipropyl ketone is the chief one, but no satisfactory proof was given. In the present work, we have repeated the former investigation and demonstrated the correctness of the assumptions made then as to the course of the reaction.

Since hydrogen chloride is developed in quantity, the assumption was made that the other product is a nitroso compound. All representatives of this class are known to possess a deep blue color; hence the formation

<sup>1</sup> Lynn, *THIS JOURNAL*, 41, 368 (1919).

of this color in the present reaction seems evidence enough, considering the raw materials used. The disappearance of this color and the precipitation of a yellow oil pointed to a change of the nitroso compound to an oxime, since it is well known that in this class of substances, unless the nitroso group is connected to a tertiary carbon atom, there is an unvarying tendency to rearrangement. A further substantiation of this is the ready hydrolysis of the product to form hydroxylamine and a volatile substance, a characteristic behavior of the oximes. We may, therefore, express the changes as



Ammonium chloride and hydroxylamine were isolated at various times as products of the reaction, the former undoubtedly being a decomposition product of the latter under the conditions of the experiment.

The volatile product was isolated in larger quantity and identified as chiefly di-*n*-propyl ketone, the other components being probably the remaining ketones from normal heptane. Furthermore, the oxime was purified and examined, its physical constants being those of butyronoxime.

### Experimental

The normal heptane<sup>a</sup> had been distilled from the oleoresin of *Pinus Jeffreyi* and was further purified by shaking it repeatedly with sulfuric acid and a subsequent distillation over sodium hydroxide. Pure nitrosyl chloride was easily prepared by passing the gases from the reaction of sodium nitrite and hydrochloric acid into sulfuric acid and gently heating the product with dry sodium chloride. Crude nitrosyl chloride was made by heating a mixture of 4 volumes of hydrochloric acid and 1 volume of nitric acid, the product as obtained consisting principally of nitrosyl chloride and chlorine. The crude reagent gave the same reactions with heptane as did the pure, so that it was of no advantage to use the first method, and the crude mixture with chlorine was employed throughout.

This mixture of nitrosyl chloride and chlorine was led into heptane until the latter was thoroughly saturated, as indicated by a very dark red-brown color. The solution was then placed directly in the sunlight, the result being an immediate evolution of large quantities of hydrogen chloride which continued for about one-half hour. Sometimes samples appeared to be boiling vigorously. Accompanying the evolution of hydrogen chloride was a decided color change from orange or reddish-brown to green or blue, the shade depending upon the degree of saturation; the color usually obtained with highly saturated solutions was a verdant or emerald green. Also, at this stage minute globules of an oil, usually light brown but sometimes dark, made their appearance.

After the reaction had proceeded thus far, hydrogen chloride ceased

<sup>a</sup> Secured through the courtesy of the Wisconsin Pharmaceutical Experiment Station.

to be given off so vigorously, the color gradually faded to either lighter shades of green or Copenhagen blue, the quantity of precipitated oil increased, and finally the color disappeared entirely, an evident sign of complete reaction. The heptane was then saturated, as previously described.

The resultant oil, light colored at first, rapidly became dark reddish-brown. It remained acid in reaction, slowly evolving hydrogen chloride and, when warm or at ordinary temperature, precipitated small quantities of feathery crystals of ammonium chloride, but when cooler a mixture of ammonium chloride and hydroxylamine hydrochloride was formed.

When 214 g. of oil had been collected, a portion (81 g.) was neutralized with barium carbonate to free it from hydrogen chloride, the oil was extracted with chloroform, and the chloroform evaporated. The dark brown oily residue was subjected to fractional distillation, the portions boiling at 80° to 140°, 140° to 180°, and 180° to 197° being collected. During the last part of the process because of the presence of a small amount of free hydrogen chloride, there was considerable decomposition, accompanied by deposition of ammonium chloride and much foaming. In spite of this, the third fraction was comparatively pure butyronoxime, as shown by the physical constants.

	Boiling point °C.	Specific gravity	Index of refraction
Butyronoxime <sup>3</sup> . . . . .	193	0.8924 (20°/4)	1.4475 (20°)
Third Fraction . . . . .	180-197	0.9257	1.444 (14.5°)

The remaining portion of the oil (133 g.) was distilled with steam, a process which completely hydrolyzed the oxime. The ketone product thus obtained was a colorless or slightly yellow liquid with an aromatic odor, very volatile, comparatively soluble in water, and with a burning acid taste. It was dried over anhydrous calcium chloride<sup>4</sup> and fractionated twice, giving the following fractions: up to 130°, 12 cc.; 130-150°, 35 cc.; 150-160°, 5 cc.; and a residue of 5 cc. Practically all of the second fraction came over between 140° and 150°. The physical constants of this fraction compared with those of dipropyl ketone are as follows.

	Boiling point °C.	Specific gravity	Index of refraction
Di- <i>n</i> -propyl ketone <sup>5</sup> . . . . .	143.52	0.8210 (14.8°/14.8)	1.40732 (22°)
Fraction 2 . . . . .	140-150	0.83826 (15.6°/15.6)	1.4125 (14.5°)

This shows fairly conclusively that the main portion consists of di-*n*-propyl ketone with the probable admixture of a small amount of its isomers.

This was further identified by conversion into the semicarbazone.

<sup>3</sup> Trapnensojanz, *Ber.*, 26, 1433 (1893).

<sup>4</sup> Curiously, calcium chloride is soluble in cold dipropyl ketone, but very slightly in the hot substance.

<sup>5</sup> Louginine, *Ann. chim.*, [7] 13, 331 (1898); Perkin, *J. Chem. Soc.*, 69, 1236 (1896); Bruhl, *J. prakt. Chem.*, [2] 50, 141 (1894).



After recrystallization from high-boiling gasoline, this had a melting point of 117°, compared with 123° for the semicarbazone from synthetic dipropyl ketone. A mixture of the two gave approximately the same melting point.

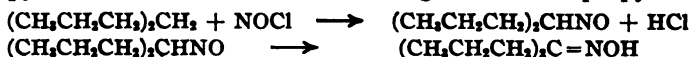
The ketone was also oxidized with potassium dichromate to give butyric and propionic acids. The oxidation mixture was distilled with steam fractionally and the fractions analyzed by means of the silver salts in the usual way. The results show the presence of butyric acid in the first and of propionic acid in the later fractions:

Silver butyrate: Ag, 55.4; silver propionate: Ag, 59.7; oxidation fractions; Ag, 54.34, 54.80, 57.82, 58.80.

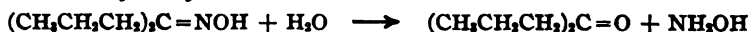
Since the results were obtained but slowly at best, an effort was made to substitute ultra-violet rays for sunlight and, also, to increase the speed of the reaction by an increase in temperature. Repeated trial has shown that the formation of nitroso compound (blue color) takes place under the influence of sunlight, at temperatures up to 80°, or with ultra-violet light. For some reason, however, the less refrangible rays of the spectrum are necessary to effect final conversion of the nitroso compound into the oxime.

### Summary

Nitrosyl chloride reacts with normal heptane in the sunlight to give di-*n*-propyl nitroso-methane, which rearranges to form dipropyl ketoxime.



Upon distillation with steam the oxime is hydrolyzed to form di-*n*-propyl ketone and hydroxylamine.



There is no record in the literature of any process in which nitrosyl chloride acts upon the paraffin hydrocarbons; hence this reaction furnishes an entirely new line of investigation. Since petroleum ether and gasoline behave similarly it is reasonable to suppose that the reaction is general for this series of hydrocarbons. Furthermore, there is every reason to expect that nitrosyl chloride will react in the same way with other compounds containing an alkyl residue. We are at present engaged in investigating the action on toluene, cymene, etc., and will report the results shortly.

SEATTLE, WASHINGTON

## NOTES

**The Reaction between *sym*-Dichloro-dimethyl Ether and Ethyl Malonate.**—A recent paper by Kamm and Waldo,<sup>1</sup> describes the condensation of  $\beta,\beta'$ -dichloro-diethyl ether with ethyl malonate, yielding a product which they designate 4,4-dicarboxyethyl-tetrahydro-pyran. This reaction is especially interesting in view of a similar experiment performed some time previous by the writers. In attempting to prepare the lower homolog containing a 4-membered oxygen heterocycle we used *sym*-dichloro-dimethyl ether and the sodium salt of ethyl malonate under conditions practically identical with those described by Kamm and Waldo. The reaction was so vigorous that cooling was necessary. Although the temperature was not allowed to exceed 50°, a copious separation of sodium chloride occurred, but the expected 2,2-dicarboxyethyl-trimethylene oxide was not formed. Instead, we obtained from 160 g. of ethyl malonate 50 g. of an oil which distilled between 185° and 190° at 6 mm. pressure, and recovered 66 g. of unchanged ethyl malonate. The oil was identified as ethyl propane-1,1,3,3-tetracarboxylate.

Subs., 0.1469, 0.1629: H<sub>2</sub>O, 0.1099, 0.1092; CO<sub>2</sub>, 0.3281, 0.3253. Calc. for C<sub>11</sub>H<sub>16</sub>O<sub>8</sub>: H, 7.28; C, 54.15. Found: H, 7.40, 7.45; C, 54.28, 54.45.

Hydrolysis of this ester, followed by expulsion of carbon dioxide by heating in an oil-bath at 200°, gave a crystalline acid with melting point 97–98° and neutralization equivalent 66. These constants correspond to those of glutaric acid.

Subs., 0.2, 0.15: H<sub>2</sub>O, 0.1102, 0.0834; CO<sub>2</sub>, 0.3312, 0.2482. Calc. for C<sub>8</sub>H<sub>8</sub>O<sub>4</sub>: H, 6.06; C, 45.45. Found: H, 6.12, 6.18; C, 45.19, 45.13.

The alcohol recovered from the first reaction had a strong ethereal odor. By repeated fractionation and salting out with calcium chloride we obtained 20 g. of an ether boiling at 88–90°,  $d_{24}^{24}$ , 0.862. These properties identify the substance as methylene diethyl ether.

It is probable that in this condensation the sodium reacts as sodium ethylate and not as the sodium salt of ethyl malonate, and that the reaction occurs in three stages as follows.

1.  $\text{ClCH}_2\text{OCH}_2\text{Cl} + \text{NaOC}_2\text{H}_5 = \text{ClCH}_2\text{OCH}_2\text{OC}_2\text{H}_5 + \text{NaCl}$ .
2.  $\text{ClCH}_2\text{OCH}_2\text{OC}_2\text{H}_5 + \text{NaOC}_2\text{H}_5 = \text{C}_2\text{H}_5\text{OCH}_2\text{OC}_2\text{H}_5 + \text{CH}_3\text{O} + \text{NaCl}$ .
3.  $\text{CH}_3\text{O} + 2\text{CH}_3(\text{COOC}_2\text{H}_5)_2 = \text{CH}_2[\text{CH}(\text{COOC}_2\text{H}_5)_2]_2 + \text{H}_2\text{O}$ .

The third stage is not quantitative, as shown by the recovery of ethyl malonate and the strong odor of formaldehyde. The reactions indicated are in agreement with the work of Kleber<sup>2</sup> who obtained ethyl propane-1,1,3,3-tetracarboxylate from monochloro-dimethyl ether and the sodium salt of ethyl malonate. Perkin<sup>3</sup> also obtained the same product from tri-

<sup>1</sup> Kamm and Waldo, *THIS JOURNAL*, **43**, 2223 (1921).

<sup>2</sup> Kleber, *Ann.*, **246**, 107 (1888).

<sup>3</sup> Perkin, *Ber.*, **19**, 1054 (1886).

oxymethylene and ethyl malonate with acetic acid as a condensing agent, and Knoevenagel<sup>4</sup> obtained it from 40% formaldehyde and ethyl malonate in the presence of a secondary amine.

Evidently in Kamm and Waldo's  $\beta,\beta'$ -dichloro-diethyl ether the ether linkage is very much more stable than in the isomeric  $\alpha,\alpha'$ -dichloro-diethyl ether or the lower homolog, *sym*-dichloro-dimethyl ether which is likewise an  $\alpha$ -derivative.

ARTHUR W. DOX AND LESTER YODER

DEPARTMENT OF CHEMICAL RESEARCH  
(PAPER No. 9)

PARKE, DAVIS AND COMPANY,  
DETROIT, MICHIGAN

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**Beta Naphthol.**—In teaching laboratory courses in organic chemistry, the writer has the conviction that not enough emphasis is being placed on the reaction in which an aromatic sulfonic acid is converted into a phenol by fusion of the sodium salt of the acid with sodium hydroxide. Lately, this reaction has become of first importance. The reaction has a wide application, and for that reason examples of it should be in our courses. In our modern laboratory manuals the preparation of  $\beta$ -naphthol which is one of the simplest and most readily made phenols, is either left out or is described by directions that will not yield the substance in good amount and of good quality.

In working with the preparation of the sodium salt of  $\beta$ -naphthalene sulfonic acid and its conversion to  $\beta$ -naphthol, certain observations not specifically mentioned in the literature have been made. These facts should be helpful to other teachers and to those engaged in research problems involving work with sulfonic acids and phenols.

After sulfonation of an aromatic hydrocarbon, the usual procedure is to neutralize the mixture with lime. This leaves the unsulfonated hydrocarbon and most of the calcium sulfate undissolved. On filtration, the filtrate contains the soluble calcium sulfonate, together with quite a little dissolved calcium sulfate. The latter will continue to crystallize from solution for at least several days.<sup>1</sup> The filtrate from the calcium sulfate contains the calcium sulfonate, and usually this solution is treated directly with a solution of sodium carbonate until the calcium is all precipitated as the normal carbonate. We have found that the only way to obtain a satisfactory precipitation at this point is to use pure anhydrous sodium carbonate from a freshly opened container. The use of the hydrated

<sup>4</sup> Knoevenagel, *Ber.*, 27, 2346 (1894).

<sup>1</sup> Namba, *J. Soc. Chem. Ind.*, 40, 281T (1921).

sodium carbonate always led to unsatisfactory results.<sup>2</sup> The sodium salt thus formed was not found to yield  $\beta$ -naphthol on fusion with sodium hydroxide. All preparations of hydrated sodium carbonate available to us seemed to contain considerable bicarbonate. This formed a soluble calcium hydrogen carbonate that was very difficult to convert to the normal carbonate. Repeated boilings and evaporations did not completely remove the carbon dioxide. The use of pure anhydrous sodium carbonate gave a product that was completely soluble in water and did not effervesce when moistened with strong mineral acid.

In the conversion of the sulfonate into the phenol, a second precaution necessary for the success of the reaction is a fusion in the absence of conditions that can oxidize the product and bring about a decreased yield. To this end, iron crucibles are avoided and commercial hydrochloric acid is not used in the recovery of the product of the fusion.

We have found the following to be the best conditions for the laboratory preparation of  $\beta$ -naphthol.

In a 75cc. nickel or silver crucible fuse 30 g. of sodium hydroxide and 3 cc. of water. Heat to  $270^\circ$  and add 10 g. of finely pulverized sodium naphthalene sulfonate that is completely soluble in water and shows the presence of no carbonates.<sup>3</sup> Gradually increase the temperature of the contents of the crucible to  $315^\circ$ . There is a tendency toward boiling over and the mixture requires slow heating. In about 20 minutes after the sodium salt has been added, the mixture reaches the latter temperature where it is allowed to remain for about 3 minutes. If the sodium salt is quite pure, no marked tendency toward boiling over will be observed. After fusion, pour the mixture onto a cement floor or table top, dissolve in water, cool slightly and acidify strongly with chemically pure hydrochloric acid. Allow the mixture to stand overnight, filter, wash with a little water and allow to dry in the funnel. The product will be only slightly colored and on sublimation will yield beautiful flakes resembling naphthalene. The above directions have been used repeatedly in our classes and give a high grade product in good yield. Almost all such fusions give lower yields than a calculation calls for, but by watching the details the yield can be increased.

DEPARTMENT OF CHEMISTRY,  
INDIANA UNIVERSITY,  
BLOOMINGTON, INDIANA  
Received August 9, 1921

CLARENCE E. MAY

<sup>2</sup> Our attention has been called lately to the fact that is not widely known perhaps, that pure anhydrous sodium carbonate left exposed to the air for several days will absorb carbon dioxide in an amount sufficient for the conversion of 20% of the original carbonate into bicarbonate. Sodium carbonate of this latter quality should not be used in converting a calcium sulfonate into a sodium sulfonate.

<sup>3</sup> We have found an ordinary army rifle shell partly filled with a high boiling paraffin serves well as a protector for the thermometer bulb. The fused sodium hydroxide dissolves some zinc out of the brass shell but one shell has been used for more than 50 fusions and is still practically unchanged.

## NEW BOOKS.

**Victor Meyer.** By RICHARD MEYER. Akademische Verlagsgesellschaft m. b. H., Leipzig, 1917. xv + 462 pp. 17 × 24.5 cm.

The book is divided into two parts. Part 1 deals with the life, and Part 2 with the work. All scientists will enjoy reading the first portion because of the intimate picture it gives of the life of a prominent scientist, and of the world he moved in. Organic chemists will give close attention to Part 2, because here we find a record of pioneer work in organic chemistry: the nitro compound of the aliphatic series, the hydroxylamines, thiophene and its derivatives, stereoisomerism, etc. The physical chemist will also read with interest the account of Victor Meyer's method of determining vapor density, and his researches dealing with the effect of high temperature.

Altogether this book is a delight to the lover of the history of chemistry. Its record of Meyer who held chairs of chemistry at Zürich, Göttingen and Heidelberg, and who was the intimate friend of Bunsen, Baeyer, Wallach, Fischer, Kekulé, and others, is well worth while.

BENJAMIN HARROW

**Chemie der Organischen Farbstoffe.** BY DR. FRITZ MAYER, A. O. Hon. Professor an der Universität Frankfurt A. M. Julius Springer, Berlin, 1921. VI + 257 pp. 5 fig. 24.5 × 16 cm. Price M. 138; bound, M. 150.

This book is intended to take the place of R. Nietzki's "Die Chemie der Organischen Farbstoffe" which has been out of print for some years. It is not an exhaustive treatise to be used solely as a reference book, but a readable and up-to-date survey of the chemistry of synthetic and natural dyestuffs. The author has succeeded in summarizing in a relatively small volume the most interesting and essential portions of a very large and complex subject. The treatment follows the orthodox lines: color and constitution, dyeing properties and coal tar refining are briefly discussed in the introduction; the usual classes of synthetic dyes are next considered and a final chapter on natural coloring materials (including the anthocyanins) concludes the book. The whole subject is presented from a very general point of view; reference is made not only to recent technical advances but also to the results of certain investigations of theoretical interest, such as the mechanism of the coupling reaction of diazonium salts and the structure of indigo. The book will be of value both to the advanced student who wishes an introduction to this important subject, and to the organic chemist who is interested in the modern developments in this field.

JAMES B. CONANT

THE JOURNAL  
OF THE  
American Chemical Society

with which has been incorporated the

American Chemical Journal  
(Founded by Ira Remsen)

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[CONTRIBUTION FROM THE KENT CHEMICAL LABORATORY OF THE UNIVERSITY OF CHICAGO]

VAPORIZATION IN STEPS AS RELATED TO SURFACE FORMATION

Seventh Paper on the Orientation of Molecules in Surfaces<sup>1</sup>

BY WILLIAM D. HARKINS AND LATHROP E. ROBERTS

Received August 20, 1921

Introduction

That the process of vaporization may occur in steps is evident. Thus, mechanical forces may cause a liquid to spread out in a thin layer, or may throw it out into sheets, or atomize it into minute drops. Any of these processes increases the proportion of the liquid in the surface, and since the molecules in the surface are more nearly in the vapor state, both in the sense of contiguity and of the energy relations involved, than those inside the liquid, surface formation may be considered as one of the steps in the process of vaporization. It is therefore evident that a part of the energy necessary for vaporization may be supplied directly in the mechanical form.

It is the purpose of the present paper to consider to what extent the different steps in the vaporization of a liquid may be evaluated in terms of energy. At all temperatures below the critical point all molecules which pass from the interior of a liquid into the vapor must pass through the surface, so the principal stages in the process of vaporization are, first, surface formation, and second, the jumping out of the molecules from the surface into the vapor. The energy of surface formation is supplied partly

<sup>1</sup> Presented in a seminar at the University of Illinois in the year 1918-19.

as heat, specified as the latent heat of surface formation, and partly in the mechanical form which gives rise to the free surface energy.

It would be very simple to determine the energy values for the steps listed above if a definite amount of liquid, as that corresponding to 1 mol of vapor, could first be drawn from the interior into the surface, and then vaporized. However, while it is very easy to do this for the total change from the interior of the liquid to the vapor, it is not so simple in the steps in which the surface is involved, since the number of molecules in the surface is not known. However the work of Langmuir,<sup>2</sup> and of Harkins and his coworkers Clark, King and Grafton,<sup>3</sup> has given extensive data on the number of molecules in surface films of organic substances on water which should enable us to make an estimate of the number of molecules in the surface of a pure liquid which, presumably, will not be very far from the actual number. When this is done it becomes possible to calculate the molar latent heat of surface formation and the molar free surface energy, and to compare these with the molar heat of vaporization. In the present paper these molar values will be divided by  $6.062 \times 10^{23}$ , thus converting them into the mean molecular values.

#### Calculation of the Energy Values for the Vaporization Steps

In estimating the number of molecules per square centimeter of surface of a liquid, the corresponding number determined in surface films on water may first be considered. These are listed for a few substances taken as examples, in Table I.

TABLE I  
NUMBER OF MOLECULES IN THE "MONOMOLECULAR FILM" ON A WATER SURFACE<sup>2,3</sup>

Substance	No. atoms carbon	No. molecules per sq. cm. $\times 10^{-14}$
1. Formic acid.....	1	(1.7)
2. Acetic acid.....	2	(2.0)
3. Propionic acid.....	3	2.6
4. Butyric acid.....	4	2.8
5. Valeric acid.....	5	(3.1)
6. Caproic acid.....	6	(3.2)
7. Heptylic acid.....	7	2.9
8. Nonylic acid.....	9	3.1
9. Decylic acid.....	10	3.3
10. Palmitic acid.....	16	4.8
11. Stearic acid.....	18	4.6
12. Cerotic acid.....	25	4.0
13. Octyl alcohol.....	8	2.9
14. Myricyl alcohol.....	30	3.7
15. Propyl formate.....	4	3.7

<sup>2</sup> The results listed for Compounds 10 to 15 in Table I, were obtained by Langmuir, *THIS JOURNAL*, 39, 1848-1906 (1917).

<sup>3</sup> The results for Compounds 1 to 9 were obtained by Harkins, Clark and King in the years 1916 to 1919, but have not previously been published.

The most complete data which have been collected for a single series of compounds are those for the acids listed in the table. The results which are inclosed in parentheses are less accurate than the others. One remarkable feature of the values is that the larger the molecule, until the number of carbon atoms reaches close to 16, the smaller the area covered. This is evidently because the attraction between the molecules in the surface film increases with their length. Since this attraction is small in the case of the shorter molecules, they spread out more over the surface of the water; but as the attraction becomes greater they are held together more closely and the orientation is more exact. However, if it were not for this effect, the larger molecules would be expected to occupy the greater surface, even when they are oriented, since, on account of their heat motion, some molecules would be doubled and turned out of their regular positions, which would increase the surface occupied. These two effects result in the appearance of a maximum number of molecules (minimum area per molecule) somewhere near 16 carbon atoms, where the number of molecules per square centimeter is  $4.8 \times 10^{14}$ . While short or small molecules may thus occupy a greater area on water by spreading out somewhat over the surface, this is not possible in the case of a pure liquid, since, if the outermost molecules spread out, the openings thus produced are filled by like molecules, so that in a pure acid or alcohol, the number of molecules per square centimeter for short molecules may be expected to be as high as or even higher than the maximum listed above.

While the molecules in the surface of a liquid may be supposed to have a random arrangement in the plane of the surface (with an orientation with respect to the perpendicular to the plane), a simplifying assumption will be introduced for purposes of calculation. This is that the number of molecules in unit area of the surface is equal to the two-thirds power of the number in unit volume. While the orientation of the molecules in the surface would cause a very lack of *space* symmetry in the case of such molecules as those of palmitic, stearic and cerotic acids, it seems evident that there are many cases in which orientation need not result in any considerable lack of symmetry of this sort. This may be illustrated most easily by the use of an analogy. Suppose a sphere to consist of one heavy and one light hemisphere, and that it rests upon a frictionless plane. It is evident that it would orient with the light hemisphere up, but that the space symmetry would be complete. Most of the molecules listed in the tables of this paper are not of the type which would be expected to depart widely in the sense of space symmetry with respect to general form, though it need not be assumed that they actually take on a spherical form; nor need it be assumed that all of the molecules in the surface lie in a plane. Some molecules undoubtedly lie higher in the surface than others, and the former will in general possess more surface energy of the potential form. The energy



TABLE II A  
ENERGY VALUES FOR THE VAPORIZATION IN STEPS OF NON-ASSOCIATED LIQUIDS

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
$T$	$\tau$	$\Gamma$ ergs cm <sup>3</sup> .	$E$ ergs cm <sup>3</sup> .	$\frac{d\Gamma}{dT}$	$A_i$ cal g.	$\frac{10^4 E}{T A_i}$	$d$	$\pi \times 10^{11}$	$\lambda$ $\times 10^{14}$	$l$ $\times 10^{14}$	$e$ $\times 10^{14}$	$i$ $\times 10^{14}$	$\lambda_i$ $\times 10^{14}$	$\frac{e}{\lambda}$	$\frac{e^{d^{1/2}}}{\lambda_i^{1/2}}$ $\times 10^{14}$	$\frac{e}{\lambda_i^{1/2}}$ $\times 10^{14}$	$\frac{e}{\lambda_i^{1/2}}$ $\times 10^{14}$
Carbon Tetrachloride $T_c = 556$																	
293	0.527	25.68	60.87	0.117	...	...	1.594	6.28	7.85	10.6	18.5	29.3	47.8	0.315	...	...	...
313	0.563	24.41	60.87	0.117	...	...	1.554	6.12	7.29	10.9	18.2	...	...	0.322	...	3.48	2.88
413	0.743	12.22	54.80	0.103	35.27	37.6	1.345	5.30	4.02	14.0	18.0	...	...	0.481	0.789	3.39	2.93
463	0.833	7.28	51.26	0.095	29.52	37.5	1.219	4.80	2.56	15.5	18.0	13.3	31.3	0.574	0.785	3.34	2.96
503	0.905	3.56	47.30	0.087	23.73	39.6	1.086	4.28	1.35	16.6	17.9	7.3	25.2	0.712	0.832	3.30	2.95
523	0.941	1.93	41.68	0.076	19.85	40.2	0.998	3.93	0.77	16.0	16.7	4.4	21.1	0.794	0.827	3.05	2.83
533	0.959	1.20	36.91	0.067	17.15	40.4	0.941	3.71	0.50	14.9	15.4	2.8	18.2	0.846	0.832	2.79	...
Diethyl Ether $T_c = 467.5$																	
313	0.670	14.05	49.1	0.112	75.02	20.9	0.6894	5.64	4.43	9.6	13.4	25.0	30.4	0.350	0.407	3.05	...
323	0.691	12.94	48.9	0.111	72.66	20.8	0.6764	5.54	4.14	11.5	15.6	21.5	37.2	0.421	0.469	3.56	3.11
373	0.798	7.63	45.5	0.102	60.4	20.2	0.6105	4.95	2.67	12.9	15.6	15.3	30.9	0.504	0.455	3.47	2.98
423	0.905	2.88	39.3	0.086	44.3	21.0	0.5180	4.24	1.10	13.9	15.0	7.6	22.7	0.662	0.472	3.28	2.29
443	0.948	1.33	32.8	0.071	34.3	21.6	0.4658	3.81	0.55	12.9	13.4	4.1	17.5	0.766	0.486	2.91	2.70
458	0.980	0.38	23.0	0.049	23.0	21.8	0.4018	3.20	0.17	10.2	10.4	1.4	11.8	0.885	0.492	2.24	...
Benzene $T_c = 561.5$																	
363	0.647	19.16	61.3	0.116	84.69	19.9	0.8041	6.25	5.65	12.4	18.1	27.5	45.6	0.396	0.530	3.42	2.83
413	0.763	13.45	59.1	0.111	73.45	19.5	0.7440	5.78	4.18	14.2	18.4	21.2	39.6	0.464	0.518	3.43	2.95
463	0.825	8.16	54.5	0.100	62.51	18.8	0.6758	5.25	2.70	15.3	18.0	15.6	33.7	0.536	0.500	3.31	2.88
513	0.914	3.41	48.1	0.087	46.53	20.1	0.5851	4.54	1.21	15.9	17.5	7.5	25.1	0.699	0.535	3.17	2.89
533	0.949	1.75	43.6	0.079	37.55	21.8	0.5328	4.14	0.68	16.2	16.9	3.3	20.2	0.836	0.579	3.05	2.79
Chlorobenzene $T_c = 63.3$																	
433	0.684	16.62	59.7	0.100	64.14	21.5	0.9480	5.11	5.73	14.9	20.6	29.2	49.8	0.414	0.584	3.43	2.89
473	0.747	12.72	58.6	0.097	58.50	21.2	0.8955	4.83	4.45	16.2	20.5	24.9	45.4	0.452	0.562	3.40	2.92
503	0.795	9.88	56.7	0.093	53.90	20.9	0.8518	4.59	3.58	16.9	20.5	21.3	41.9	0.491	0.555	3.37	2.95
533	0.842	7.14	53.8	0.088	48.17	21.0	0.8016	4.32	2.69	17.6	20.3	18.0	38.3	0.530	0.543	3.30	2.93
Ethyl Acetate $T_c = 524$																	
363	0.693	15.14	57.6	0.117	76.40	20.8	0.8112	5.58	4.81	13.5	18.3	28.1	46.4	0.394	0.495	3.72	3.18
413	0.788	9.57	53.8	0.107	64.42	20.2	0.7378	5.08	3.24	15.0	18.2	21.0	39.2	0.465	0.482	3.62	3.15
463	0.864	4.54	47.6	0.093	49.48	20.8	0.6441	4.43	1.68	15.9	17.6	12.5	30.1	0.587	0.495	3.45	3.08
483	0.922	2.80	43.1	0.084	42.08	21.2	0.5944	4.09	1.09	15.8	16.8	8.8	25.6	0.669	0.505	3.26	2.95
503	0.960	1.18	35.9	0.069	31.32	22.8	0.5281	3.64	0.50	14.7	15.2	3.8	19.0	0.798	0.542	3.92	2.86

TABLE II B																	
ENERGY VALUES FOR THE VAPORIZATION IN STEPS OF MERCURY AND OF ASSOCIATED LIQUIDS																	
Methyl Formate $T_c=48.7$																	
313	0.643	21.56	68.8	0.151	101.1	21.7	0.9447	9.54	4.79	10.5	15.3	26.8	42.1	0.363	0.544	3.36	2.87
363	0.745	14.29	65.5	0.141	85.25	21.2	0.8634	8.72	3.37	12.1	15.5	19.8	35.3	0.438	0.533	3.33	2.85
413	0.848	7.54	60.4	0.128	68.10	21.5	0.7638	7.71	1.93	13.5	15.5	12.7	28.2	0.548	0.540	3.28	2.90
443	0.910	3.90	53.7	0.113	54.41	22.3	0.6844	6.91	1.08	13.7	14.8	7.7	22.5	0.657	0.561	3.10	2.78
436	0.951	1.78	46.2	0.096	41.93	23.8	0.6148	6.21	0.53	13.2	13.7	3.7	17.4	0.787	0.599	2.84	2.64
Nitrogen $T_c=127$																	
70	0.551	10.53	26.63	0.230	44.85	84.8	0.8446	18.27	1.51	2.32	3.84	4.83	8.67	0.442	0.717	3.32	2.75
80	0.630	8.27	25.87	0.220	41.72	77.5	0.7988	17.28	1.24	2.63	3.87	4.20	8.07	0.480	0.656	3.29	2.85
88	0.693	6.57	24.61	0.205	39.00	71.7	0.7622	16.49	1.01	2.79	3.80	3.74	7.54	0.504	0.608	3.16	2.74
Oxygen $T_c=154.2$																	
70	0.454	18.35	36.90	0.265	48.95	107.6	1.2393	23.47	2.24	2.26	4.50	6.31	10.81	0.416	1.058	3.23	...
78	0.506	16.25	36.53	0.260	48.10	97.4	1.2008	22.75	2.13	2.53	4.55	6.07	10.62	0.428	0.956	3.24	2.70
84	0.545	14.72	35.64	0.255	47.56	89.2	1.1719	22.20	1.86	2.72	4.56	5.94	10.50	0.434	0.884	3.18	2.70
Methyl Alcohol $T_c=51.3$																	
363	0.708	15.72	49.5	0.093	232.1	5.9	0.7250	13.72	2.74	5.9	8.6	42.7	51.3	0.168	0.192	1.62	1.39
413	0.805	10.79	54.4	0.106	195.4	6.7	0.6640	12.57	2.00	8.1	10.1	33.1	43.2	0.233	0.220	1.95	1.64
463	0.903	5.23	59.4	0.117	147.5	8.7	0.5770	10.82	1.06	11.0	12.1	20.5	32.6	0.370	0.284	2.38	2.13
483	0.942	2.93	58.0	0.114	119.5	10.1	0.5255	9.95	0.63	11.9	12.5	13.9	26.4	0.475	0.329	2.47	2.19
503	0.981	0.77	47.5	0.093	74.6	12.7	0.4410	8.35	0.19	11.4	11.6	4.9	16.5	0.700	0.414	2.26	...
Ethyl Alcohol $T_c=516.1$																	
333	0.645	18.43	48.7	0.091	199.2	7.3	0.7572	9.97	3.98	6.54	10.5	52.8	63.3	0.166	0.209	1.97	1.61
383	0.742	13.69	51.8	0.100	174.9	7.7	0.7057	9.29	3.10	8.62	11.7	43.8	55.6	0.211	0.225	2.25	1.88
433	0.839	8.45	55.4	0.109	141.7	9.0	0.6329	8.34	2.06	11.42	13.5	31.6	45.0	0.299	0.263	2.64	2.30
473	0.917	3.99	56.3	0.111	104.0	11.5	0.5568	7.33	1.06	13.85	14.9	18.2	33.0	0.449	0.332	2.93	2.64
Water $T_c=647$																	
283	0.437	71.94	109.0	0.131	559.3	6.9	0.9997	33.63	6.90	3.56	10.5	59.1	69.6	0.150	0.344	1.26	1.22
333	0.515	64.27	120.2	0.168	525.4	6.9	0.9834	33.09	6.24	5.43	11.7	53.7	65.3	0.179	0.343	1.63	1.40
383	0.592	55.25	128.8	0.192	489.2	6.9	0.9512	32.00	5.48	7.20	12.8	48.1	60.8	0.210	0.343	1.91	1.70
Acetic Acid																	
423	0.711	14.46	51.0	0.087	82.37	14.6	0.8963	9.05	3.33	8.42	11.8	22.3	34.1	0.344	0.449	1.99	1.66
463	0.779	10.93	53.1	0.091	77.97	14.7	0.8413	8.49	2.63	10.13	12.8	19.5	32.3	0.395	0.452	2.19	1.86
503	0.846	7.28	54.1	0.093	71.44	15.0	0.7764	7.84	1.85	11.87	13.7	15.9	29.6	0.463	0.462	2.36	2.06
543	0.913	3.59	51.6	0.089	60.37	15.8	0.6900	6.97	0.98	13.16	14.2	10.8	25.0	0.565	0.483	2.48	2.15
563	0.947	1.92	46.1	0.079	50.32	16.3	0.6334	6.39	0.56	12.82	13.4	7.5	20.9	0.642	0.500	2.28	2.06
Mercury ( $T_c=1500?$ )																	
313	(0.208)	479.7	552.6	0.233	69.58	253.7	13.497	40.79	40.48	6.16	46.6	49.7	96.3	0.484	13.2	1.97	1.45
363	(0.242)	468.0	552.6	0.233	68.77	221.3	13.376	40.42	39.73	7.18	46.9	48.3	95.2	0.493	11.4	1.98	1.50
413	(0.275)	458.4	552.6	0.233	67.97	196.8	13.257	40.06	38.97	8.22	47.2	46.9	94.1	0.501	10.2	1.99	1.50
443	(0.295)	449.4	552.6	0.233	67.48	184.8	13.186	39.85	38.54	8.85	47.4	46.0	93.4	0.506	9.6	2.00	1.55

TABLE II B  
ENERGY VALUES FOR THE VAPORIZATION IN STEPS OF MERCURY AND OF ASSOCIATED LIQUIDS

values in the tables are intended to be as nearly the arithmetical mean values as it is now possible to determine them. That the assumption used as the basis for the calculation is of value will be seen from the remarkable relations which emerge.

At  $20^\circ$  the calculations indicate the presence of  $4.2 \times 10^{14}$  molecules of ethyl alcohol per sq. cm., while the results on films of alcohol on water show that when the film is closely packed the number of molecules is very close to  $4.0 \times 10^{14}$ , or the same number as that found for the pure alcohol.

### Notation

The symbols used in Table II have the following significance.

$T$  = absolute temperature.

$\tau = T/T_c$ , where  $T_c$  is the critical temperature.

$\Gamma$  = surface tension in ergs per cm., or free surface energy in ergs per sq. cm.

$\gamma$  = free surface energy in ergs per area occupied by one molecule.

$S$  = entropy of surface in ergs per degree per sq. cm.

$s$  = entropy of surface in ergs per degree per constant area equal to the area occupied by one molecule at the definite temperature specified.

$s'$  = the same as  $s$  but calculated for a changing area equal to that occupied by one molecule at the different temperatures, internal latent heat of vaporization in calories per gram.

$\frac{10^4 E}{T}$  Whittaker's constant.

$\frac{ed^3/s}{x \tau}$  molecular capillary constant.

$d$  = density of liquid.

$n$  = number of molecules per cc. of liquid.

$n_s$  = number of molecules per sq. cm. of surface.

$l$  = latent heat of the area of surface occupied by one molecule in  $10^{-14}$  ergs.

$e$  = total surface energy of same area or the surface energy per molecule in  $10^{-14}$  ergs.

$j$  = energy changed from kinetic to potential when one molecule jumps from the surface into the vapor (in  $10^{-14}$  ergs), or the molecular energy of thermal emission.

$L$  = latent heat of the surface per sq. cm.

$E$  = total energy of the surface per sq. cm.

$\Delta_i$  = internal latent heat of vaporization per mol.

$\lambda_i$  = mean internal latent heat of vaporization per molecule.

### Defining Equations

$$e = \gamma + l$$

$$\lambda = e + j = \gamma + l + j$$

$$\gamma = \frac{\Gamma}{n_s}$$

$$l = \frac{L}{n_s}$$

TABLE II C

ENERGY VALUES FOR THE VAPORIZATION IN STEPS OF NON-ASSOCIATED LIQUIDS AT ORDINARY TEMPERATURES (ENERGY VALUES IN MICRI-ERGS  $10^{-14}$  ERGS)

$T$	$T/T_c$	$d$	$n_s \times 10^{-14}$	$e$	$j$	$\lambda$	$e/\lambda$
$=\pi$ Carbon Tetrachloride $T_c = 556$							
255	0.459	1.659	3.496	18.5	37.2	55.66	0.333
273.1	0.491	1.632	3.458	18.0	35.6	53.58	0.337
298	0.526	1.585	3.392	17.1	33.6	50.72	0.338
308	0.554	1.560	3.356	16.4	33.2	49.57	0.331
328	0.590	1.525	3.305	16.6	29.5	46.12	0.361
Ethyl Ether $T_c = 467$							
198	0.424	0.818	3.552	15.2	36.4	51.59	0.295
252	0.541	0.758	3.376	15.0	30.3	45.32	0.332
273.2	0.585	0.735	3.307	15.4	37.5	42.94	0.358
283.9	0.607	0.723	3.271	12.7	29.0	41.71	0.304
298.3	0.639	0.707	3.223	12.8	27.3	40.05	0.293
302.5	0.647	0.703	3.210	11.8	27.8	39.57	0.298
Benzene $T_c = 561.5$							
278.4	0.496	0.895	3.64	21.6	33.3	54.9	0.393
282.5	0.503	0.889	3.63	20.8	33.5	54.3	0.382
298.1	0.531	0.873	3.58	19.5	33.3	52.8	0.369
308.1	0.549	0.862	3.55	18.2	33.5	51.7	0.353
328	0.585	0.841	3.49	17.3	32.2	49.5	0.350
347.6	0.619	0.817	3.43	17.6	29.7	47.3	0.373
Chlorobenzene $T_c = 363$							
257	0.406	1.144	3.362	20.9	48.8	69.7	0.299
273	0.431	1.128	3.33	21.0	46.9	67.9	0.310
298	0.471	1.101	3.28	21.9	43.2	65.1	0.336
308	0.486	1.090	3.26	22.3	41.6	63.9	0.349
323	0.510	1.073	3.22	22.4	39.8	62.2	0.360
343.5	0.543	1.051	3.18	22.6	37.3	59.9	0.378
363	0.574	1.029	3.13	22.9	35.9	58.8	0.390
375	0.592	1.016	3.11	23.0	33.3	56.3	0.409
387.5	0.612	1.003	3.08	23.2	31.7	54.9	0.423
395	0.624	0.995	3.07	23.3	30.7	54.0	0.431
Ethyl Acetate $T_c = 524$							
213	0.406	0.999	3.61	18.4	44.6	63.0	0.292
243	0.464	0.961	3.52	18.7	40.9	59.7	0.314
273	0.521	0.924	3.43	17.7	38.6	56.4	0.314
303	0.578	0.887	3.34	16.0	37.1	53.1	0.302
333	0.636	0.847	3.24	14.7	35.1	49.8	0.295

Note to Table II. The surface tension values for nitrogen and oxygen are those of Baly and Donnan [*J. Chem. Soc.*, 81, 919 (1902)]. The values for nitrogen were calculated by Planck [*Physik. Z.*, 11, 642 (1910)] from results by Bestelmayer and Valentin [*Ann. Physik*, 15, 61 (1901)]; Baly and Donnan, and Alt. [*Sitz. Bayer. Akad. Wiss.*, 22, 529 (1903) and *Physik. Z.*, 6, 346 (1903)].

The values for the internal latent heat of vaporization of oxygen were calculated by the writers from the vapor-pressure data of Estreicher [*Phil. Mag.*, [5] 40, 454 (1895)].

The constants of the Hertz equation were determined graphically. The equation for nitrogen is

$$\text{Log } p = k_1 - k_2 \log T - \frac{k_3}{T}$$

where  $k_1$  is 8.455,  $k_2$  is 0.64847, and  $k_3$  is 392.84.

The values of  $dp/dt$  for mercury were obtained from the equation given by Menzies:

$$\log p = 9.9073 - 0.65199 \log T - \frac{3276.6}{T}$$

and the values of  $p$  and  $T$  were taken from Smith and Menzies [THIS JOURNAL, 32, 1412 (1910)].

In the case of carbon tetrachloride and similar other liquids, use was made of the values of the latent heat of vaporization calculated by Mills [THIS JOURNAL, 32, 164 (1910)]. However, all of the values of the latent heat of vaporization used in Table II C, were calculated by the writers.

Table II as given above is a condensed outline of a much more elaborate table calculated by the writers, and contains enough data to illustrate the characteristic features of the relations. The surface tension data used in Parts A and B are those of Ramsay and Shields,<sup>4</sup> in Part C those of Jaeger, and the vapor-pressure data from which the internal heats of vaporization were obtained, are those of Young,<sup>5</sup> except when otherwise specified. *Practically all of the experimental data cited in the literature, which give the variation of the surface tension of liquids with the temperature, were plotted and carefully compared.* These were largely results obtained by Ramsay and Shields, Morgan, Jaeger, Renard and Guye, Walden, and those obtained in this laboratory. The data on organic liquids as obtained by Ramsay and Shields covered on the whole the largest temperature range, and were mostly in moderately good agreement with our own data, as well as those of Morgan, though they are in general about 3% too low at 20°, as is shown by the experimental results obtained both by Richards and his coworkers, and by the workers in the Chicago laboratory. If the results are consistently too low by this percentage, the latent surface heat would not be all in error on this account, and this percentage difference in the free surface energy would make little difference to the results of the calculations as presented in Table II.

In comparing the surface tension data of Jaeger, as given in Table II C, with those of Ramsey and Shields, it is found that the distinguishing feature of the latter is that the surface tension for unassociated liquids is nearly always found to be a linear function of the temperature, while the surface-tension data obtained by Jaeger are nearly always such as to show considerable curvature. A comparison with other data indicates that probably the latter are too highly curved. On the other hand those of Ramsay and Shields seem to be considerably more linear than is probable, but nevertheless they seem to be in better agreement with the other data than those of

<sup>4</sup> Ramsay and Shields, *Z. physik. Chem.*, 12, 433 (1893).

<sup>5</sup> Young, *Sci. Proc. Roy. Dublin Soc.*, 12, 374 (1910).

Jaeger, which seem to show considerable irregularity. Seemingly Jaeger's method is better designed for the determination of surface tension at high and low temperatures, than it is for the finding of temperature coefficients.

### Ratio of the Total Surface Energy to the Latent Heat of Vaporization

It has been commonly accepted by those who have considered at all, the connection between the energy of surface formation and the heat of vaporization, that the relation developed by Stefan<sup>6</sup> in 1886 is approxi-

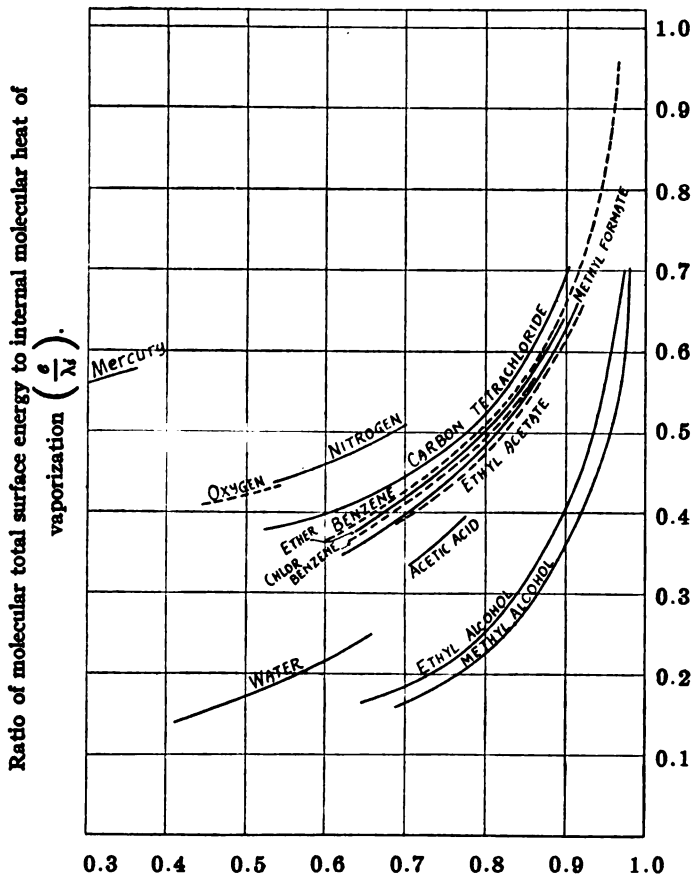


Fig. 1.—Corresponding temperature.

mately correct. Stefan considers that the work of carrying a molecule into a surface is one-half of the energy of vaporization ( $\lambda$ ). It seems evident that what is meant by Stefan is not the "work" or free energy ( $\gamma$ ), but rather the mean total energy required to carry the molecule

<sup>6</sup> Stefan, *Wied. Ann.*, 29, 655-65 (1896).

from the interior of the liquid to the surface ( $e$ ). However, the calculations presented in Table II are not at all in agreement with the relation of Stefan, since they indicate that *the ratio of the molecular total surface energy to the molecular heat of vaporization ( $e/\lambda$ ) is an increasing function with increasing corresponding temperature, since the molecular surface energy remains nearly constant until the critical temperature is approached, that is until the corresponding temperature rises nearly to 1.00, while the molecular heat of vaporization decreases very rapidly with increasing temperature.* (See Fig. 1.) Thus in the sense of the relative amounts of energy involved a molecule which is in the surface of a liquid at a high temperature has passed much more nearly into the vapor than when the temperature is low. While this is true in general, the details involved necessitate considerable discussion, and this will be presented in a somewhat elementary form in the following paragraphs.

In considering the surface energy relations involved, the surface energy per square centimeter ( $E$ ), instead of the molecular value ( $e$ ) will be considered first. It has been shown by Jaeger<sup>7</sup> that there are three types of curves which represent the relation between the free surface energy ( $\Gamma$ , plotted on the Y axis) and the temperature (plotted on the X axis). These are (1), concave, (3) convex to the temperature axis, and (2) which is a straight line. Harkins, Davies and Clark<sup>8</sup> showed that corresponding to these there are three curves representing the total surface energy, (1) rising to a maximum near the critical temperature, (2) remaining constant till the critical temperature is approached, and (3) constantly decreasing. All of these decrease rapidly near the critical temperature and come to zero at the critical temperature; and this is also the case with the curve which would represent the latent heat of vaporization. Only when the total energy curve has the form (3) would it be possible that the Stefan relation should hold, and even in this case it would probably never happen that the curve would have the precise form essential for this purpose. While it is true that for the data now available Type 3 is the most common, it may nevertheless be seen from the table that the total surface energy does not decrease so rapidly as the latent heat of vaporization, so the ratio  $E/\lambda$ , increases with the temperature.

### The Molecular Total Surface Energy

The molecular total surface energy ( $e$ ) is very nearly constant at low temperatures (curve of Type 2) in the case of the nonassociated liquids listed in Table II A, B (see Fig. 2) though there is little doubt that in some instances it rises to a maximum, and then falls, as the temperature increases. Quite a number of substances which show this characteristic, have been

<sup>7</sup> Jaeger, *Verslag. Akad. Wetenschappen Amsterdam*, 23, 416-30 (1914).

<sup>8</sup> Harkins, Davies and Clark, *THIS JOURNAL*, 30, 551-86 (1917).

investigated by Jaeger, and acetic acid is shown by Table II B to belong to this class. The data for the alcohols indicate that the molecular surface energy rises rapidly as the critical temperature is approached, reaching

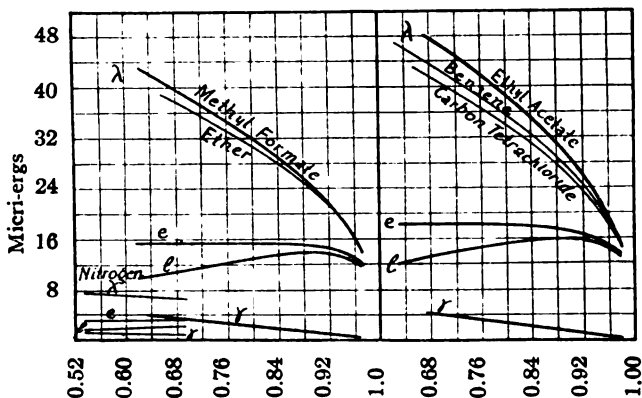


Fig. 2.—Corresponding temperature.

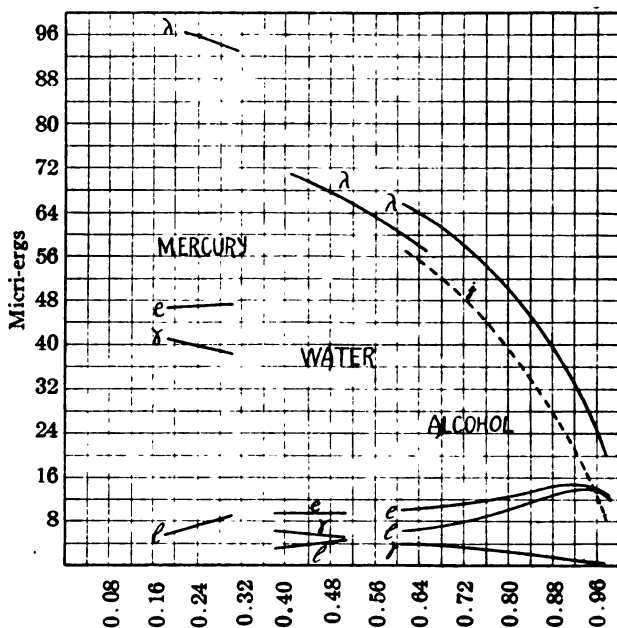


Fig. 3.—Corresponding temperature.

maximum close to 0.9, and then falls still more rapidly (Fig. 3). If this is true it may be explained as the result of the heat motion of the molecules, which, as the temperature increases, more and more overcomes the orienta-



tion in the surface of these unsymmetrical molecules, thus throwing the polar end of the molecules into the surface, thereby increasing the surface energy. However, as the critical temperature is approached still more closely, the vapor begins to increase rapidly in density, and the drop in the intensity of the electromagnetic stray field which occurs at the surface is thus lessened, so the surface energy again decreases.

The vertical position of the curves in Figs. 2 and 3 is based upon the assumption that the surface film is monomolecular. There is much evidence, both that presented by Langmuir and that secured in this laboratory, that this is true at a corresponding temperature of 0.5. At the critical temperature, however, the film has thickened so greatly that it has swallowed up both the liquid and the vapor phases. The form of the curve for the total surface energy depends upon how rapidly the film thickens as the corresponding temperature approaches unity, but it seems likely that the greatest part of the thickening occurs very close to the critical temperature, especially as the linear character of the curve representing free surface energy commonly persists to corresponding temperatures somewhat above 0.9. However, the vertical position of the  $\epsilon$  curves at temperatures above 0.8 should be considered doubtful, and in Figs. 2 and 3 it seems practically certain that the extreme right hand end of these curves should all be lowered somewhat from the positions which they occupy. The position and shape of the right end of these curves in the diagram are also indications that possibly they should turn downward a little to the left of the actual point of inflection, since the  $\epsilon$  curves can never rise above those for  $\lambda_i$ , and must come to zero when  $\tau$  rises to unity. However, this change would not alter the *general features* of the relationships involved, and it is believed by the writers that these are well represented by the figures. It would have been possible, of course, to have made an allowance for this factor in drawing the curves, and this possibility was carefully considered; but on account of the uncertainty in regard to the temperature at which the thickening of the film becomes of importance, it was decided to draw the figures so that they would give a more direct representation of the experimental results, and to point out the direction in which they will undoubtedly be modified by later work.

#### Molecular Symmetry, and the Orientation of the Molecules in Surfaces as Related to the Ratio of the Surface Energy to the Heat of Vaporization ( $\epsilon/\lambda_i$ )

The earlier papers of this series have shown that when a molecule consists of a polar group, such as OH, NH<sub>2</sub>, COOH, CONH<sub>2</sub>, CN, etc., at one end of the chain, and a slightly polar group, such as a hydrocarbon chain, its action with respect to the energy changes on passing into the surface may be predicted by the use of a model which consists of a heavy weight

at one end while the other end is made from some light material. This model may be represented by the symbol  $\text{---}\circ$ , in which  $\circ$  represents weight. When a molecule of this class is raised into the surface it is only the "light" end which is lifted, so the surface energy ( $e$ ) is relatively small, while when the molecule jumps out of the surface the "heavy" end must be lifted out, so the "jumping-out energy" or the energy of thermal emission ( $j$ ) is relatively large. As an example of this latter type of molecule we may choose that of ethyl alcohol. In the case of a symmetrical molecule, such as that of carbon tetrachloride, it is to be expected that the energy of surface formation and that of thermal emission from the surface will be very much more nearly the same. It will be shown later that it is essential that different liquids shall be compared at the same corresponding temperatures.

For convenience the energy unit for use in the present paper will be taken as  $10^{-14}$  erg. In order to prevent the frequent use of the negative exponent this unit will be specified as a micri-erg. A micro-erg is a millionth of an erg, and the new unit is one hundred million times smaller than this. The term micri-erg has no philological justification, but the Greek terms which would be justified in this sense are considerably more awkward for common use.<sup>9</sup>

At a corresponding temperature equal to 0.743 the mean amount of energy required to carry a molecule of carbon tetrachloride from the interior of the liquid into the surface is 18.0 micri-ergs, while the energy of thermal emission or that used up in causing it to jump out of the surface into the vapor is almost the same, or 19.4 micri-ergs. If instead of this very symmetrical molecule we consider the molecule of ethyl alcohol, which is very unsymmetrical with reference to the electrical forces around it, it is found that the energy ( $e$ ) required to carry the molecule into the surface is only about one-half as great, or 11.7 micri-ergs, while the jumping-out energy or energy of thermal emission is more than doubled, and has the remarkably high value 43.8 micri-ergs. *The energy of thermal emission for the alcohol is thus four times the energy of surface formation, while in the symmetrical carbon tetrachloride, the two are almost equal.*

The corresponding values for the methyl alcohol molecule are almost exactly the same as those for ethyl alcohol, while those for benzene are nearly the same as those for carbon tetrachloride. If we assume that the ratio  $e/j$  may be used as an index of the symmetry of the molecules in the surface, then the values are such as to indicate that in this sense the benzene molecule is slightly less symmetrical than that of carbon tetrachloride, which is exactly what would be expected from the formulas. The values of the ratio  $e/j$  for a number of different types of molecules are given in Table III.

<sup>9</sup> The distinction between micro and micri may be easily preserved if the final i in the latter is pronounced as a long i.

Instead of plotting the values of  $e/j$ , which would be somewhat more striking with respect to the relations disclosed, it seemed better from other standpoints to plot  $e/\lambda$ , as has been done in Fig. 3. This ratio has already been discussed to some extent. Since  $e/\lambda$  is equal to  $\frac{e}{e+j}$ , it is evident that if the value of  $e/j$  increases with increasing symmetry of the molecule, then that for  $e/\lambda$  will also increase, though not so markedly. Table III gives 13 liquids arranged in the increasing order of  $e/\lambda$ , which according to the preceding discussion should on the whole be that of increasing symmetry of the molecules in the surface.

TABLE III  
LIQUIDS ARRANGED IN THE ORDER OF THE RATIO OF THE ENERGY NECESSARY TO CARRY A MOLECULE INTO THE SURFACE TO THAT REQUIRED FOR COMPLETE VAPORIZATION, AND PRESUMABLY IN ORDER OF INCREASING SYMMETRY IN THE SURFACE  
(CORRESPONDING TEMPERATURE = 0.7)

Molecule	$e/\lambda$	$e/j$
Class 1		
1. Methyl alcohol.....	0.164	0.191
2. Ethyl alcohol.....	0.186	0.228
Class 2		
3. Water.....	0.282	0.372
4. Acetic acid.....	0.336	0.474
Class 3		
5. Ethyl acetate.....	0.397	0.606
6. Methyl formate.....	0.402	0.618
7. Chlorobenzene.....	0.417	0.714
9. Ethyl ether.....	0.423	0.667
10. Benzene.....	0.441	0.711
11. Carbon tetrachloride.....	0.452	0.742
Class 4		
12. Oxygen.....	0.497	0.872
13. Nitrogen.....	0.514	0.927
Class 5		
14. Mercury.....	0.636	1.41

The important feature of this table is that the arrangement is not only such as to group chemically similar substances together, but also that it actually gives the expected order of increasing symmetry of the molecules with reference to the forces around them. This is shown both by the arrangement of the classes of substances, and by the arrangement of the substances in the classes. Thus in Class 3, the order ethyl acetate, methyl formate, chlorobenzene, ethyl ether, benzene, and carbon tetrachloride, is very plainly that of increasing symmetry of the forces around the molecule. Minor variations might easily be caused by small errors in the data, or by errors in the determination of the number of molecules in the surface. However, Table III proves that these errors are not sufficient to obscure the general relationships.

As has already been stated, Stefan's "law" states that the energy of surface formation is equal to half the energy of vaporization, but it was shown that instead of being constant, the ratio is an increasing function with increasing temperature. Table III and Fig. 1 indicate that this ratio is also an increasing function with increasing symmetry of the molecules. It may be seen in Table II that at a corresponding temperature of 0.7, the different liquids are from 0.16 to 0.64 vaporized, in terms of energy. At lower temperatures all of these values decrease, while at higher temperatures they increase, this increase being very rapid as the critical temperature is approached. The curves in Fig. 1 seem to have a form such as to indicate that the ratio  $e/\lambda$  approaches its maximum 1.00 at the critical temperature, which would mean that at temperatures very slightly below this nearly all of the energy is utilized in carrying the molecules from the body of the liquid into the surface, and that the energy of thermal emission from the surface is very small. Thus these curves seem to have the same general form in approaching the critical temperature, which is the limit for the existence of the liquid, as is found for the specific heat curves when they approach the absolute zero of temperature, which is the limit for the existence of heat. The experimental determination of either curve near its limit is in either case a matter of extreme difficulty.

### The Energy of Thermal Emission of a Molecule from the Surface of a Liquid

The energy of thermal emission ( $j$ ) of a molecule from the surface of a liquid into the vapor, has values ranging from about 4 to 50 micri-ergs at corresponding temperatures between 0.4 and 0.98, in the case of the liquids listed in Table II. In all cases the value decreases very rapidly as the temperature increases. The variation with the temperature is very much the same as that of the molecular free surface energy, except that as the critical temperature is approached closely the free surface energy decreases more slowly while the energy of emission decreases more rapidly. In the case of chlorobenzene the value for the latter decreases by 11.2 micri-ergs between 0.68 and 0.84 as the corresponding temperatures, but this decrease is nearly linear, while the increase of the free surface energy is almost exactly linear, and the value of the molecular surface energy is nearly constant at 20.5 micri-ergs. In general the curve for  $j$  is slightly concave toward the  $\tau$  axis, but usually not so much so as the curve for  $\lambda$ , as may be seen in Fig. 3.

As has already been pointed out, the energy of thermal emission is particularly high in the case of molecules of the polar-nonpolar type, such as the alcohols, which are highly polar at one end and "non-polar" at the other. This should be true also of the amines, nitriles, etc. Its value is larger for the alcohols than for water. While the total energy

necessary to carry a molecule of mercury into a surface is about four times as high as that required for an ethyl alcohol molecule at the same corresponding temperature, the energy of thermal emission is only slightly higher for the former. The value for acetic acid is very much lower, which is partially accounted for by the fact that the vapor of this substance is somewhat associated. The total surface energy is increased very little, and the energy of thermal emission, considerably, when one atom of chlorine is substituted for hydrogen in benzene, as would be expected from the orientation theory.

### The Surface Energy Constant

If the ratio  $e/\lambda_i$ , which increases rapidly with a rise of the corresponding temperature, is multiplied by the ratio  $d^{2/3}/\tau$ , the product  $\frac{e d^{2/3}}{\lambda_i \tau}$  is found to be nearly constant for nonassociated liquids and seems to be very nearly constant over a moderate range in the case of water. It rises rapidly with the temperature in the case of the unsymmetrical molecules of the alcohols. The value for mercury is very high. Whittaker's constant, given in Col. 7 of Table II applies to the large scale properties of the substances, and varies in about the same way.

### Summary

1. This paper gives the amount of energy involved in the various steps in the process of vaporization, based upon the assumption that the surface through which the vaporization occurs is not highly curved. The unit of energy used is the *micri-erg*, defined as  $10^{-14}$  erg. The relations found at a corresponding temperature equal to 0.7 are summarized in brief in Table IV.

TABLE IV  
MOLECULAR ENERGY VALUES (IN MICRI-ERGS) FOR THE VAPORIZATION OF LIQUIDS AT A CORRESPONDING TEMPERATURE EQUAL TO 0.7

LIQUID	$T_c$	$\gamma$	$l$	$e$	$j$	$\lambda_i$
1. <i>Non-associated</i>	Molecular = $\tau$					
Nitrogen.....	127	1.51	2.33	3.84	4.8	8.7
Oxygen.....	154.2	2.24	2.26	4.50	6.1	10.8
Ethyl ether.....	467.5	4.0	11.7	15.6	20.9	36.5
(Ethyl acetate).....	(524)	(4.6)	(13.7)	(18.3)	(27.7)	(46.0)
Carbon tetrachloride....	556	4.7	13.5	18.2	22.0	40.2
Benzene.....	561.5	4.8	13.7	18.4	23.3	41.7
Chlorobenzene.....	633	5.3	15.0	20.3	28.5	48.8
2. <i>Associated</i>						
Methyl alcohol.....	513	2.8	5.7	8.5	43.1	51.6
Ethyl alcohol.....	516.1	3.5	7.7	11.2	48.1	59.3
		(4.4)	(12.5)	(16.9)	(20.4)	(37.3)

The data indicate that at a definite corresponding temperature, in the case of non-associated liquids whose molecules are symmetrical, the molecular

values for the latent heat of surface formation ( $l$ ), the total surface energy ( $e$ ), the energy of thermal emission ( $j$ ), and the internal latent heat of vaporization ( $\lambda_i$ ) are nearly proportional to the critical temperatures of the liquids. The same relation seems to hold for the free surface energy ( $\gamma$ ) provided the temperature range is not too great. Thus the free surface energy of ethyl ether at a corresponding temperature of 0.7 is 4.0 as calculated from the value for carbon tetrachloride, and 3.9, as calculated from the value for chlorobenzene, while the experimental value is 4.0. This statement as applied to the latent heat of vaporization alone, is somewhat similar to Trouton's law, which is known to be not entirely exact. Since the principle expressed above is much more general in its application, it is to be expected that it will prove to be somewhat less exact. That the energy values for ether in Table IV are lower than those for carbon tetrachloride is related to the lower critical temperature of the ether.

2. *The effect of a lack of symmetry in the molecule, especially when marked, is to lower the molecular free surface energy, latent heat of surface formation, and total surface energy, and to increase the energy of thermal emission.* The values given in parentheses under those for ethyl alcohol, are those calculated from the critical temperature under the assumption of a symmetrical molecule, using the values for carbon tetrachloride as a basis. It is evident that the molecular free surface energy, and total surface energy, and more markedly the latent heat of surface formation, are considerably lowered by the dissymmetry of the molecule. The most striking effect is, however, the very great increase in the energy of thermal emission. The symmetry referred to in this discussion is that of the electromagnetic forces around the molecule, rather than a symmetry with respect to mass. The substitution of the slightly polar chlorine atom for hydrogen in benzene gives almost exactly the calculated value for a symmetrical molecule except in the case of the thermal emission ( $j$ ), which is considerably increased, since it is the most sensitive of all of the quantities to changes of molecular symmetry. Since  $e$  is decreased, and  $j$  increased by increasing dissymmetry of the molecule, the ratio  $e/j$  serves as a remarkably sensitive index of molecular symmetry. This is illustrated in Table III.

The related ratio  $e/\lambda$ , which is equal to  $\frac{e}{e+j}$ , varies in the same way, but not so greatly.

3. According to "Stefan's law" the ratio of the total energy necessary to carry a molecule from the interior of a liquid into the surface to its total heat or energy of vaporization ( $e/\lambda$ ) is equal to  $1/2$ . That this is not the case is easily seen by a reference to Tables II and III, and Fig. 1. Not only is this an increasing function with increasing symmetry of the molecule, but also with increasing corresponding temperature. Its value seems to approach unity as the corresponding temperature approaches unity.

Thus a molecule in the surface at a high corresponding temperature is, in terms of relative energy, very much more nearly in the vapor phase than when the corresponding temperature is low.

4. The relations discussed in Paragraphs 1 and 2 of the summary are just those indicated by the theory that molecules in the surface are oriented, the orientation increasing with increasing dissymmetry, and decreasing with increasing thermal agitation of the molecules. The effect of thermal agitation is illustrated in the case of the alcohols; compounds of the polar-nonpolar type. Fig. 3 indicates that for these compounds the molecular surface energy increases with the temperature. The effect of increased agitation is to overcome the orientation partly, and to throw the more polar groups into the outer surface, thus increasing the surface energy.

CHICAGO, ILLINOIS

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF MISSOURI]

## IONIC EQUILIBRIA OF STRONG ELECTROLYTES

BY ALLEN E. STEARN

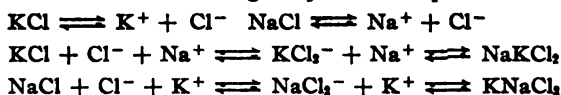
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### I

The ionic relationships in relatively concentrated solutions of mixed strong electrolytes have been studied especially by Smith<sup>1</sup> and his students, who have shown that, as the total concentration of a salt mixture of equivalent amounts of two salts increases, the ion fraction of one of the metallic constituents gains on the ion fraction of the other. Recently Kendall<sup>2</sup> has attacked the problem of "complex formation" between solute and solvent.

### II. Conductivity of Concentrated Solutions

When such salts as sodium and potassium chlorides are mixed in solution such equilibria as the following may be set up.



The formation of such molecular or ion complexes in solution, causing the gain of one ion fraction on another<sup>3</sup> in a salt mixture, should decrease the conductivity of such a solution of mixed salts. Thus the conductivity of an equimolar solution of sodium and potassium chlorides of a

<sup>1</sup> G. McP. Smith, *Am. Chem. J.*, **37**, 506 (1907). Smith and Ball, *THIS JOURNAL*, **39**, 179 (1917). Smith and Braley, *ibid.*, **40**, 1802 (1918). Wells and Smith, *ibid.*, **42**, 185 (1920).

<sup>2</sup> Kendall, *ibid.*, **39**, 2328 (1917); **43**, 1416 (1921); **43**, 1426 (1921).

<sup>3</sup> Noyes and Falk have suggested the existence of  $\text{SrCl}_4$ , etc., in solution from the results of transference experiments. *Ibid.*, **33**, 1455 (1911).

total concentration of one equivalent per liter should be less than that calculated from the conductivities of solutions of the pure salts each at the same concentration as the above total concentration. From the isohydric principle we should expect the values obtained in these two ways to be the same. The strongest experimental support of this principle has been derived from conductivity studies although other properties have been studied in connection with it. The writer has studied the heats of dilution<sup>4</sup> of mixed salt solutions, finding that they deviated from values calculated on the basis of this principle. Bender,<sup>5</sup> from a study of expansion coefficients, concluded that on mixing salt solutions these coefficients are not the arithmetical mean but that the concentration can be so adjusted as to give this value. Such solutions, having the same expansion coefficients, he termed "corresponding solutions." Doroshevskii and Dvorzhanshik<sup>6</sup> besides studying the conductivities of dilute mixed salt solutions, found that the refractive indexes of the very dilute solutions of salts of sodium and potassium with the same anion were identical.

For dilute solutions the effect of complex formation on the conductivity may be expected to be very small; in fact for a total concentration of 0.1 *N*, the upper limit for a majority of conductivity studies, Smith<sup>1</sup> postulates equal ion fractions of  $\text{Na}^+$  and  $\text{K}^+$  in an equimolar mixture of sodium and potassium chlorides. The effect should vary with varying total concentrations. The value of this effect on conductivity may be expected to be small, however, for such ions as  $\text{NaCl}_2^-$ ,  $\text{KCl}_2^-$ ,  $\text{Na}_2\text{Cl}_3^-$ ,  $\text{K}_2\text{Cl}_3^-$ ,<sup>7</sup> etc., will be highly polar particles and, indeed, may well be of such a nature as to respond easily to the "parting effect" of a weak electrical field,<sup>8</sup> even though this field alternates in sign periodically.

<sup>4</sup> Stearn and Smith, *THIS JOURNAL*, **42**, 18 (1920). Smith, Stearn and Schneider, *ibid.*, **42**, 32 (1920).

<sup>5</sup> Bender, *Wied. Ann.*, **27**, 179 (1884).

<sup>6</sup> Doroshevskii and Dvorzhanshik, *J. Russ. Phys. Chem. Soc.*, **45**, 1174 (1913).

<sup>7</sup> We should expect to find sodium the more "noble" metal in the anion according to the usual theory of complex ions, which would mean that, as the total concentration of an equimolar  $\text{NaCl} + \text{KCl}$  solution increased, the potassium-ion fraction should gain on the sodium-ion fraction. As a matter of fact, however, Smith [*THIS JOURNAL*, **35**, 39 (1913)] and Smith and Ball [*ibid.*, **39**, 179 (1917)] have shown from a study of the heterogeneous equilibria between aqueous and metallic solutions, that as the total concentration increases, the sodium-ion fraction actually gains on the potassium-ion fraction. No generally satisfactory explanation as to the cause of this seeming anomaly, which indicates a preponderance of complex anions containing potassium instead of sodium, seems to have been offered.

<sup>8</sup> Cf. Harkins, *Proc. Nat. Acad. Sci.*, **6**, 601 (1920). He suggests that for the degree of dissociation or ionization different measurements, giving different results on the same solution, should be interpreted in different ways. Thus  $\text{NaIO}_3$  in solution may be 100% ionized (meaning merely 100% polarized), 85% electrolytically dissociated (*i. e.*, 85% of the molecules have their polar parts far enough apart to respond to an electric field



The effect of complex formation on conductivity may be further decreased by probable ion dehydration. Thus the value of the hydration of the chlorine ion at infinite dilution given by Smith<sup>9</sup> is 9 and for the potassium ion it is 9.6. At higher concentrations these values will, of course, be smaller, but at any concentration, if  $m$  is the number of molecules of water of hydration of the chlorine ion and  $n$  the number for the potassium ion, then to obtain the fullest possible effect of complex ion formation on conductivity we should require a hydration of at least  $2m + n$  molecules of water for a  $KCl_2^-$  ion. This, however, is highly improbable, and thus any dehydration would tend to increase the mobility of the complex and mask the effect of complex formation on the conductivity.

By definition, equivalent conductivity ( $\Lambda$ ) is the reciprocal of the resistance of a quantity of solution containing one equivalent of electrolyte, measured between parallel electrodes 1 cm. apart. In practically all the determinations made up to this time the solutions studied have been made up by volume and thus any mass effect of the solvent has been neglected. In the case of dilute solutions the values obtained for volume-normal or weight-normal<sup>10</sup> will not differ appreciably, but in the case of concentrated solutions the mol fraction of one salt in a volume-normal solution will not be the same as that of any other salt at equivalent-volume normality, and any volume change on mixing solutions would interfere with the comparability of results. Previous work on concentrated solutions of mixed electrolytes<sup>11</sup> has not taken this into account, and the difference between the observed and calculated values for these solutions has been assumed to be due to experimental error as it has not been consistently of the same sign. For these reasons, in this work the equivalent conductivities of weight-normal solutions were measured and the specific gravities of the same solutions determined by pycnometer. In this way any mass effect of the solvent was constant and any volume changes on mixing solutions have no effect on the comparability of the results.

With such solutions, then, we may look for some effect which, even though, as pointed out above, we may expect to be small, should be consistent in sign, and may be expected to increase with increasing total concentration and become distinctly measurable at higher concentrations. Those up to 4  $N$  were used in this work.

or potential gradient as "free" ions in contradistinction to "bound" ions), while perhaps only 68% is thermodynamically dissociated.

<sup>9</sup> Smith, *THIS JOURNAL*, 37, 722 (1915).

<sup>10</sup> *I. e.*, one equivalent of solute per 1000 g. or 55.5 formula weights of  $H_2O$ .

<sup>11</sup> MacGregor, *Proc. Royal Soc. Canada*, [2] 4, 117 (1898). MacGregor, Archibald, McIntosh and McKay, *Trans. Nova Scotia Inst. Sci.*, 9 and 10 (1895-99).

## Materials

**Salts.**—The salts used were the chlorides, bromides and iodides of sodium and potassium. c. p. salts were recrystallized once, and dried at about 200°. Before using, each was heated until decrepitation ceased.

**Solutions.**—The chloride solutions could be made up by weighing proper quantities of salts and water. The bromides and iodides were too hygroscopic for this, and so a large quantity of the 4 *N* and of the *N* solutions of the pure salts was made up by weighing the previously heated salt from a stoppered bottle and adding the proper weight of water. The solutions of mixed salts and other concentrations of the pure salts were made by mixing weighed quantities of these solutions with the proper weighed quantities of water.

**Conductivity Water.**—The most dilute solution studied was 0.1 *N* and its specific conductivity is comparatively high. Nevertheless, conductivity water was prepared by the usual method of distilling the ordinary distilled water from alkaline permanganate and then from very dil. sulfuric acid and condensing by means of block tin or silica condensers. Both kinds were used. All the water used had a specific conductivity between  $1 \times 10^{-8}$  and  $2 \times 10^{-8}$  mhos.

## Apparatus and Procedure

The usual conductivity apparatus was employed. It consisted of a Kohlrausch bridge with extension coils, a 5-dial Curtis-coil resistance, a constant-speed high-frequency generator and tunable telephone.<sup>12</sup> Kohlrausch cells were used, varying in constant from about 7 to about 50 for the more concentrated solutions. Some of the work was done with a cell having adjustable electrodes and the same solution thus run in a series of "cells." The cell constants were determined with a normal solution of pure potassium chloride. The capacities of the cells were balanced by variable air condensers across the terminals of the resistance.

The specific conductivities of the solutions were measured at  $25^\circ \pm 0.02^\circ$ , and from the determined specific gravities the volumes containing one gram-equivalent of solute were calculated and the equivalent conductivity thus obtained.

The solutions used were those of sodium and potassium chlorides and mixed chlorides in the molecular proportions  $2\text{NaCl} : \text{KCl}$ ,  $\text{NaCl} : \text{KCl}$ , and  $\text{NaCl} : 2\text{KCl}$ , with total equivalent concentrations of 0.1 *N*, 0.25 *N*, 0.5 *N*, 1 *N*, 2 *N*, and 4 *N*. The same concentrations of bromides and iodides were also run, except that 3 *N* solutions were also included.

## Results

Table I gives the equivalent conductivities,  $\Lambda$ , for the chlorides, bromides and iodides, respectively. For the mixed salts the calculated and observed values are both given and also their difference. With the formation of complexes the observed value should be less than that calculated on the basis of the isohydric principle and the differences in this direction are called positive, in the other direction are called negative. They are termed  $\Delta\Lambda$ .

Table II gives the values of the specific gravities of the various solutions employed. They are referred to water at 4° and corrected for the buoyancy of air.

<sup>12</sup> All furnished by the Leeds and Northrup Company.

TABLE I  
EQUIVALENT CONDUCTIVITIES  
Chlorides

Conc. N	NaX	$\Lambda$ KX	$\Lambda$ 2NaX:KX		$\Delta\Lambda$	$\Lambda$ NaX:KX		$\Delta\Lambda$	$\Lambda$ NaX:2KX		$\Delta\Lambda$
			Calc.	Obs.		Calc.	Obs.		Calc.	Obs.	
0.10	106.82	128.34	113.99	114.12	-0.13	117.58	117.46	0.12	121.16	120.97	0.19
0.25	100.11	121.98	107.40	107.02	0.38	111.05	110.69	0.36	114.69	114.58	0.11
0.50	93.92	117.06	101.63	101.51	0.12	105.50	105.16	0.35	109.35	109.10	0.25
1.00	86.36	111.60	94.77	94.14	0.63	98.98	98.75	0.23	103.19	102.82	0.37
2.00	75.90	105.70	85.83	85.17	0.66	90.80	90.12	0.68	95.77	95.20	0.57
3.00	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....
4.00	60.11	96.25	72.16	71.21	0.95	78.18	77.06	1.12	84.20	83.31	0.89
Bromides											
0.10	110.60	130.95	117.70	117.82	-0.12	120.78	120.84	-0.06	124.00	124.20	-0.20
0.25	103.42	126.55	111.13	110.83	0.30	115.00	114.68	0.32	118.85	118.70	0.15
0.50	97.86	120.90	105.53	104.91	0.62	109.38	108.90	0.48	113.22	113.10	0.12
1.00	90.60	117.20	99.57	99.04	0.53	103.90	103.30	0.60	108.30	107.88	0.42
2.00	80.50	111.10	90.70	90.28	0.42	95.80	95.26	0.54	100.90	100.52	0.38
3.00	72.39	105.96	83.58	82.67	0.91	89.17	88.30	0.87	94.77	94.03	0.74
4.00	64.85	101.09	76.93	75.52	1.41	82.50	81.63	0.97	89.01	87.95	1.06
Iodides											
0.10	109.40	130.56	116.50	116.60	-0.10	120.00	120.15	-0.15	123.50	123.50	0.00
0.25	104.10	127.00	111.75	111.43	0.32	115.50	114.96	0.54	119.40	119.30	0.10
0.50	98.83	122.20	106.62	106.20	0.42	110.50	110.12	0.38	114.40	114.11	0.29
1.00	92.53	118.58	101.21	100.68	0.53	105.55	104.90	0.65	109.89	109.55	0.34
2.00	83.66	113.69	93.67	93.02	0.65	98.67	98.10	0.57	103.68	103.15	0.53
3.00	75.76	109.08	86.87	86.00	0.87	92.42	91.70	0.72	97.97	97.30	0.67
4.00	68.36	103.74	80.15	79.36	0.79	86.05	85.20	0.85	91.95	90.70	1.25

TABLE II  
SPECIFIC GRAVITIES  
Solutions of pure sodium halide

Conc. <i>N</i>	Chloride	Bromide	Iodide
4.00	1.1357	1.2707	1.3856
3.00	....	1.2084	1.3012
2.00	1.0710	1.1424	1.2058
1.00	1.0363	1.0724	1.1061
0.50	1.0172	1.0350	1.0520
0.25	1.0073	1.0160	1.0243
0.10	1.0012	1.0042	1.0105
Solutions of pure potassium halide			
4.00	1.1513	1.2792	1.3890
3.00	....	1.2191	1.3063
2.00	1.0806	1.1497	1.2107
1.00	1.0410	1.0764	1.1092
0.50	1.0197	1.0375	1.0540
0.25	1.0087	1.0172	1.0254
0.10	1.0017	1.0054	1.0108
Solutions containing two mols of sodium to one mol of potassium halide			
4.00	1.1413	1.2722	1.3857
3.00	....	1.2107	1.3012
2.00	1.0747	1.1443	1.2059
1.00	1.0378	1.0731	1.1054
0.50	1.0180	1.0353	1.0523
0.25	1.0079	1.0161	1.0244
0.10	1.0015	1.0045	1.0105
Solutions containing one mol of sodium to one mol of potassium halide			
4.00	1.1437	1.2743	1.3864
3.00	....	1.2144	1.3029
2.00	1.0767	1.1461	1.2083
1.00	1.0384	1.0740	1.1072
0.50	1.0185	1.0358	1.0526
0.25	1.0081	1.0165	1.0248
0.10	1.0014	1.0048	1.0106
Solutions containing one mol of sodium to two mols of potassium halide			
4.00	1.1459	1.2770	1.3889
3.00	....	1.2167	1.3058
2.00	1.0780	1.1476	1.2103
1.00	1.0394	1.0754	1.1084
0.50	1.0188	1.0370	1.0535
0.25	1.0082	1.0168	1.0253
0.10	1.0015	1.0048	1.0106

Table III gives values of  $\Delta\lambda$  per 100 mhos conductivity at the different concentrations.

The 3 curves are plotted from data taken from Table V. The effect is small, even at the higher concentrations, but with the exception of the more dilute solutions its sign is consistently positive and it increases fairly consistently with the concentration. If the totals in the above table

TABLE III

Conc. <i>N</i>	$\Delta\Delta$ Chlorides			$\Delta\Delta$ Bromides			$\Delta\Delta$ Iodides		
	2Na:K	Na:K	Na:2K	2Na:K	Na:K	Na:2K	2Na:K	Na:K	Na:2K
0.10	-0.11	0.10	0.16	-0.10	-0.05	-0.16	-0.08	-0.12	0.00
0.25	0.35	0.33	0.10	0.27	0.28	0.13	0.29	0.47	0.08
0.50	0.12	0.33	0.23	0.60	0.45	0.11	0.40	0.35	0.25
1.00	0.66	0.24	0.36	0.53	0.60	0.40	0.53	0.63	0.31
2.00	0.78	0.76	0.60	0.47	0.57	0.38	0.70	0.58	0.52
3.00	..	..	..	1.10	0.99	0.79	1.01	0.79	0.68
4.00	1.33	1.45	1.07	1.87	1.18	1.20	1.00	1.00	1.38
Totals	3.13	3.21	2.52	4.74	4.02	2.85	3.85	3.70	3.22

be taken to represent the tendency toward complex formation, Table IV shows the evident tendency toward complex formation for the different metal ratios and also for the different halides.

TABLE IV

2Na:K	Na:K	Na:2K	Chlorides	Bromides	Iodides*
11.72	10.93	8.59	8.86	8.73	8.29

\* The values for the 3.00 *N* solutions of the bromides and iodides are omitted from these last three totals in order to compare them with the chlorides.

The first three figures in this table are easily explained on the basis of the results obtained by Smith and his students who have found that it is the potassium which has the greater tendency to go into the anion.

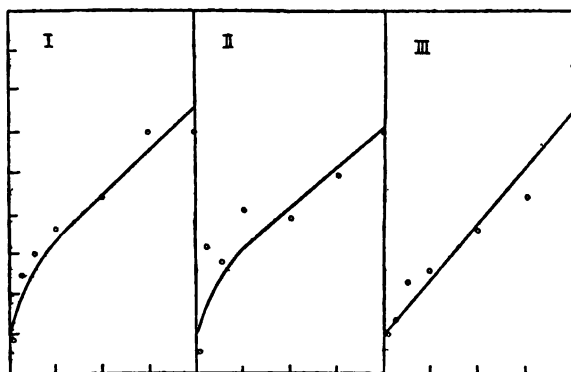


Fig. 1.—Concentrations plotted as abscissas and values of  $\Delta\Delta$  plotted as ordinates. These curves are plotted from data in Table IV for the iodides. Curve I represents the molecular mixture 2NaI:KI; Curve II, NaI:KI; and Curve III, NaI:2KI.

Thus we should expect the mass effect of the sodium to be significant and this indeed seems to be the case. The last three figures, however, indicate a decreasing tendency toward complex formation as we go from chlorides to iodides, whereas the opposite tendency has been shown to

hold.<sup>13</sup> In an attempt to account for this seeming anomaly the viscosities of some of the more concentrated solutions of the chlorides and iodides were measured. The relative viscosities of these solutions are given in Table VII. They were run at 25°, and compared to water at the same temperature. A Washburn viscosimeter was used, but as the total time of flow was only from 28 seconds to as low as 17 seconds for certain of the heavier solutions of low viscosity, the values are only approximate. They do indicate, however, that the positive values of  $\Delta\lambda$  obtained are not due merely to an increase in viscosity on mixing salt solutions, as in most cases there is an actual decrease. This decrease, however, seems greater for chlorides than for iodides, though of course the actual viscosities are much greater in case of the former. And this difference, instead of explaining the above mentioned anomaly, tends quantitatively to augment it.

TABLE V  
VISCOSITIES

Solution	4.00 N	2.00 N	1.00 N
NaCl.....	1.443	1.142	1.050
2NaCl : KCl.....	1.257	1.088	1.023
NaCl : KCl.....	1.219	1.061	1.014
NaCl : 2KCl.....	1.140	1.034	0.997
KCl.....	1.063	0.988	0.971
NaI.....	1.244	1.071	1.022
2NaI : KI.....	1.147	1.020	0.998
NaI : KI.....	1.097	0.999	0.984
NaI : 2KI.....	1.058	0.979	0.985
KI.....	0.987	0.937	0.944

There seems to be "some other tendency superimposed upon complex-ion formation to make this progression go the wrong way," and at present this is unexplained, though it is hoped that the results of some work now in progress at the University of Illinois on transference in mixed salt solutions may throw some light on the matter. The atomic volumes of the three halogens are not far apart and relatively larger velocities of iodide complexes may result from relatively greater dehydration tendency than with the bromides or iodides.

### Summary

1. Equivalent conductivities of solutions of the halides of sodium and potassium of varying weight normal concentrations were determined at 25°.
2. The observed values for the mixed salt solutions were compared with those calculated from the values for the pure salt solutions at equivalent total concentrations on the basis of the isohydric principle.
3. The difference between the calculated and the observed values

<sup>13</sup> Wells and Smith, *THIS JOURNAL*, **42**, 185 (1920).

were found to be positive and to increase with total salt concentration, with the numerical value of the ratio of sodium to potassium salt in the mixture, but to decrease generally as one goes from chlorides to iodides.

4. In general the results can be explained on the basis of complex formation, though at present no explanation is offered for the seeming decrease in complex formation proceeding from chlorides to iodides.

5. Tables of specific gravities of the solutions studied, and the relative viscosities of certain of these solutions are given.

It is a pleasure to acknowledge my thanks to Dr. George Shannon Forbes for helpful comments on certain of the results.

COLUMBIA, MISSOURI

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[CONTRIBUTION FROM THE WOLCOTT GIBBS MEMORIAL LABORATORY, HARVARD UNIVERSITY]

## THE EFFECT OF CHANGING HYDROGEN-ION CONCENTRATION ON THE POTENTIAL OF THE ZINC ELECTRODE

BY THEODORE W. RICHARDS AND THEODORE DUNHAM, JR.

Received December 14, 1921

When a metal of weak basic character (such as gallium) is studied with regard to its single electrode potential, the salt solutions in which the metal is immersed must be acidified to prevent hydrolysis. The possible effect on the potential of such acidification has not been adequately ascertained.<sup>1</sup> Accordingly, this paper recounts a brief study of the effect of adding acid to the salt solution around a typical easily and exactly reproducible metal electrode, in order to demonstrate experimentally the sign and magnitude of the potential difference thus caused. Zinc was chosen for the purpose. The results were merely preliminary, and were inevitably not very conclusive. Nevertheless, when, as here, theory is incomplete, even tentative experimental results may be of value.

Earlier papers on this subject are as follows. Broughton<sup>2</sup> studied the decomposition voltage of zinc sulfate solutions in the presence of acid, but since he made his measurements with a flowing current, the *fall* of potential which he observed was due (as he saw) to the decrease of resistance of the solution. For the present purpose these results have no significance. A. Siemens<sup>3</sup> measured the potential of zinc in an acid solution, but not in pure zinc sulfate. Details are lacking, moreover, as to salt-bridges and other particulars, so that these results also have little signifi-

<sup>1</sup> Since the completion of our experimental work a general but rather vague theoretical discussion of this matter by A. Smits has been published in "Die Theorie der Allotropie," (Barth, Leipzig, 1921), especially on pp. 176 and 399. Apparently our results are not inconsistent with his conclusions.

<sup>2</sup> Broughton, *Met. Chem. Eng.*, 20, 155 (1919).

<sup>3</sup> Siemens, *Z. anorg. Chem.*, 41, 249 (1904).

cance. Kistiakowsky<sup>4</sup> and Horsch<sup>5</sup> made accurate measurements of the electrode potential of zinc in solutions of zinc sulfate at various temperatures, but do not seem to have added acid, neither do others who have called attention to precautions needed to obtain exact results.<sup>6</sup>

The zinc employed in our work was a very pure specimen,<sup>7</sup> containing only 0.005% of known impurity, according to careful analysis. Zinc sulfate was prepared from this metal and recrystallized twice after standing in solution for 2 days over excess of zinc. From a carefully prepared molal solution of this salt and a concentrated, standardized solution of sulfuric acid, equivalent normal solutions of zinc sulfate containing various amounts of sulfuric acid were prepared. A small Leeds and Northrup potentiometer measuring to 0.1 mv. was used; it was adjusted with a cadmium cell standardized at the Bureau of Standards.

Since in such measurements solution-junction potentials are inevitable, (unless indeed some other electrode whose potential changes with added acid, such as mercury, mercurous sulfate, zinc sulfate plus sulfuric acid, be linked with the zinc electrode) the effort was made to arrange the apparatus so as to have these definite and reproducible. A separatory funnel attached by a T-tube to each narrow junction-tip made it possible to flush the latter with fresh solution whenever desired. A third separatory funnel made possible the renewal or change of the enclosed bridge solution (which received the two junction-tips) keeping the whole apparatus closed during the operation. Flow from one vessel to the other (with consequent mixture of the liquids) was prevented. By gentle hydrostatic pressure on the contents of the bridge vessel, the liquid junctions could be forced somewhat back into the narrow tubes—a process which favored reproducibility.<sup>8</sup> Each electrode vessel was removed, rinsed and dried in an oven between successive trials. The measurements were all made at  $18.0^\circ \pm 0.1^\circ$ .

Nearly all the measurements were made with amalgamated zinc. This was prepared in various ways: by immersing the metal in dilute mercurous nitrate, by rubbing the clean zinc with mercury in the air, and by amalgamating under dilute nitric acid. The methods gave essentially identical results, but the last named method seemed on the whole to give the most constant values. The rods were suspended in such a way that the metal of the connecting wire (usually platinum) was not in contact with the solution. Since zinc forms no solid amalgam, the potential of pure zinc should be identical with that of the saturated liquid amalgam;

<sup>4</sup> Kistiakowsky, *Z. Elektrochem.*, **14**, 113 (1908).

<sup>5</sup> Horsch, *THIS JOURNAL*, **41**, 1787 (1919).

<sup>6</sup> Mellencamp, *Phys. Rev.*, **29**, 329 (1909). Richards and Forbes, *Carnegie Inst. Pub.*, **56**, 1 to 45 (1906). Moore, *THIS JOURNAL*, **43**, 81 (1921).

<sup>7</sup> Kindly provided by the New Jersey Zinc Company.

<sup>8</sup> Doubtless the flowing liquid junction of Lamb and Larson, *THIS JOURNAL*, **42**, 229 (1920), would have given still more satisfactory results, but the arrangement above specified was accurate enough for our purpose.



and under the best conditions this is nearly the case.<sup>9</sup> If the electrode is not amalgamated, however, the result may be vitiated by bubbles of hydrogen as well as by the freshly formed zinc sulfate, when acid is present. Thus in the presence of 2 *N* sulfuric acid we found that the potential of a pure zinc electrode was diminished 6.5 mv. as compared with an amalgamated electrode. When the electrode is too heavily amalgamated, zinc dissolved from the surface of the amalgam may not be instantly replaced by diffusion from the solid zinc rod and the results suffer. Light amalgamation prevents active corrosion of the metal and at the same time leaves a film of mercury so thin that it remains essentially saturated with metallic zinc.

Sometimes the constant final value of the potential attained by such electrodes was several millivolts above the value obtained immediately on immersion. Evidently time was required for the attainment of equilibrium within the film, but the potential finally became constant within  $\pm 0.1$  mv. Time should doubtless be allowed that the metal may be transformed superficially into the enantiotropic form most stable at 18°,<sup>10</sup> if any of the metastable form is present; but this change can hardly be the cause of the effect observed, since it should cause a fall of potential, whereas we usually observed a rise during the first 24 hours.

Two series of experiments were made. In Series I the zinc (about half immersed in solutions containing *N* zinc sulfate, with varied amounts of added acid) was measured against a calomel electrode through a bridge of saturated solution of sodium sulfate (which was chosen because of its considerable specific gravity, helpful in diminishing diffusion at the liquid junction). In Series II the bridge-vessel was filled with *N* zinc sulfate solution, and the acidified zinc electrode was thus measured directly against another zinc electrode immersed in equivalent normal zinc sulfate without any acid, in order to simplify (as much as possible) the liquid-junction potentials. Here the only liquid-junction potential was due to the presence of acid on one side and not on the other. Zinc sulfate was used (rather than the chloride) because it forms only 2 ions on dissociation, and because it is less hydrolyzed than the chloride. No especial precaution was taken against the oxygen of the air, since results of very high precision were not sought.

The last two columns show the increase of potential due to adding acid to the solution around the amalgamated zinc electrode as measured with, and also without, a sodium sulfate bridge. Evidently, the presence of this bridge in connection with the calomel electrode tends, in every case,

<sup>9</sup> Richards and Lewis, *Proc. Am. Acad.*, **34**, 98 (1898).

<sup>10</sup> Cohen, *Proceedings Kon. Akad. Wetenschappen Amsterdam*, **16**, 565 (1913).

TABLE I  
CHANGE OF POTENTIAL OF ZINC CAUSED BY ACIDIFYING ENVIRONMENT  
 $N \text{ ZnSO}_4; N \text{ H}_2\text{SO}_4$

<i>N</i>	Total Potential <sup>11</sup> With bridge and calomel electrode	Change of potential	
		I. With $\text{Na}_2\text{SO}_4$ bridge	II. Without $\text{Na}_2\text{SO}_4$ bridge
		Mv.	Mv.
0.0	1.0777	0.0	0.0
0.1	1.0828	5.1	6.0
0.5	1.0971	19.4	21.6
1.0	1.1066	28.9	32.6
2.0	1.1173	39.6	45.3
4.0	1.1277	50.0	57.2
0.0 again	1.0771	(-0.6)	0.0

to reduce by about 12% the difference of potential observed, within the limit of error of the measurements.

The fact stands out that, with or without a salt-bridge, the addition of acid very decidedly *raises* the single electrode potential of zinc. This result is in the direction indicated by the hypothesis of electrolytic dissociation. Adding sulfuric acid to zinc sulfate should diminish the dissociation of the latter, and therefore should tend to diminish the concentration of active zinc in the solution and hence increase the potential of the electrode. The change is, however, much larger than one would expect from this cause. Hence part of the effect must be ascribed to the solution-junction potential, and most of this must be ascribed to the effect of the high mobility of the hydrogen ion. Lack of knowledge as to the concentration of the bivalent sulfate ion in sulfuric acid prevents the application to this junction potential of the equations of Planck or of Lewis and Sargent or of Henderson, but on any assumption evidently the presence of the hydrogen ion would increase the potential of the electrode containing it, since its rapid migration would tend to establish a potential difference in the same direction as that produced by the formation of the ionized zinc at the electrode. Although no accurate theory for this junction potential exists, the effect may be estimated approximately by the substitution in the present case of less rapidly migrating ions for hydrogen, making the assumption that the associating effect produced by alkali sulfates would be not very different from that produced by sulfuric acid. Accordingly, cells were set up with sodium or potassium sulfate added to the zinc sulfate solution on one side, the latter salt being always of equiva-

<sup>11</sup> The single electrode potential of zinc thus determined is 0.518, assuming the calomel electrode potential = 0.560 volt, if the electrolyte is normal as to zinc sulfate and making no allowance for the two liquid-junction potentials. The cell  $\text{Zn}, \text{ZnSO}_4, \text{KCl}, \text{HgCl}, \text{Hg}$  has an e.m.f. of about 1.083 at 18°. Saturated  $\text{Na}_2\text{SO}_4$  as a bridge diminishes the e.m.f. by about 0.005. See also Horsch, Ref. 5.

lent normal concentration. Limited solubility prevented, of course, the use of very concentrated solutions of the alkali salts. The following table gives the rise of potential observed with increasing amounts of these substances, as measured against a pure zinc electrode (equivalent normal as to zinc sulfate and without any addition of foreign sulfate).

TABLE II  
EFFECT OF DISSOLVED HYDROGEN, SODIUM AND POTASSIUM SULFATES ON THE ZINC ELECTRODE (*N* ZnSO<sub>4</sub>)

Added sulfate	H <sub>2</sub> SO <sub>4</sub>	Na <sub>2</sub> SO <sub>4</sub>	K <sub>2</sub> SO <sub>4</sub>
<i>N</i>	Mv.	Mv.	Mv.
0.0	0.0	0.0	0.0
0.1	6.0	1.7	3.2
0.5	21.6	7.2	12.1
1.0	32.6	11.8 <sup>12</sup>	..
2.0	45.3	17.1	..

These results are plotted (Curves A, C, and D) together with the values obtained with the sodium sulfate salt bridge and calomel electrode (Curve B) in the accompanying diagram. As was anticipated, the ordinates

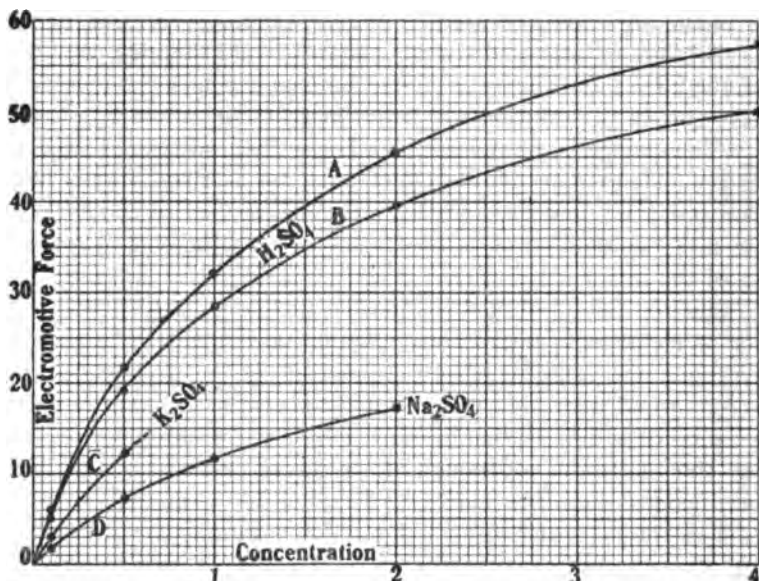


Fig. 1.—Rise of potential caused by addition of sulfuric acid and two sulfates to the normal zinc electrode. The normality of the added sulfate in the solution is plotted in the direction of abscissa; e.m.f. in millivolts, as ordinates. The concentration of zinc sulfate was normal: the same in all cases. Curve B was obtained through a salt bridge; Curves A, C, and D by direct connection with a zinc electrode surrounded by pure *N* zinc sulfate solution.

<sup>12</sup> Abegg and Labendzinski report 9 mv. for this datum, *Z. Elektrochem.*, 10, 77 (1904).

of the  $(\text{H}_2, \text{K}_2, \text{Na}_2)\text{SO}_4$  curves lie in the order of the transport numbers of the respective cations in the sulfate solutions. This is seen in the table below. From recent data,<sup>13</sup> the probable values of these transport numbers in halieds are as follows.

	Transport numbers	Relative ordinates of curves
H.....	0.83	1.00
K.....	0.49	0.56
Na.....	0.39	0.33

In concentrated solutions, the mobility of the sulfate ion is much less than that of the potassium ion, but possibly somewhat more than that of the sodium ion.<sup>14</sup> Assuming the absence of junction potential with sodium sulfate, one would infer that the difference between this salt (Curve D) and the acid (Curve A), that is, about  $\frac{2}{3}$  of the effect of the added acid, may be due to the excess of mobility of the hydrogen. The effect of sodium sulfate, 0.007 volt, when both salts are normal, is about the change of potential at the metallic surface which one would expect from the associating effect of sulfuric acid on zinc sulfate. It would appear, therefore, that well-known tendencies are of magnitudes entirely adequate to account for the total effect. Moreover, the order of magnitude of the deviation generally to be expected in other similar cases is indicated. The more exact elucidation of the question involves a better knowledge of the solution-junction effect as well as of the mode of dissociation of sulfuric acid than is now at hand. We have obtained a variety of additional data bearing upon junction potentials, but these have not yet been correlated.

We are indebted to the Carnegie Institution of Washington and to a generous anonymous fund for some of the apparatus employed.

### Summary

1. Measurements of the potential of zinc in acid solutions of zinc sulfate, measured against the calomel electrode (through a sodium sulfate bridge) and also directly against a zinc electrode containing pure *N* zinc sulfate solution, showed marked rise in potential as the acid concentration was increased.

2. The magnitude of this rise in potential indicated that it must be due partly to liquid-junction potential, owing to the presence of the hydrogen ion.

3. Equal concentrations of the sulfate ion in the form of alkali sulfates added to the zinc sulfate solution gave smaller elevations in the potential,

<sup>13</sup> A. A. Noyes and Falk, *THIS JOURNAL*, 33, 1456 (1911).

<sup>14</sup> See, for example, Kohlrausch and Holborn, "Leitvermögen der Elektrolyte," Teubner, 1898, p. 200.

which elevations were in the order of the transport numbers of the cations concerned. If it is assumed that the change in junction potential produced by sodium sulfate is small, one may infer that about  $\frac{2}{3}$  of the change produced by sulfuric acid is due to solution-junction potential and the other third to a real increase in the single electrode potential of zinc, due presumably to the depression of the electrolytic dissociation of zinc sulfate.

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[CONTRIBUTION FROM THE WOLCOTT GIBBS MEMORIAL LABORATORY, HARVARD UNIVERSITY]

## THE HEATS OF NEUTRALIZATION OF POTASSIUM, SODIUM AND LITHIUM HYDROXIDES WITH HYDROCHLORIC, HYDROBROMIC, HYDRIODIC AND NITRIC ACIDS, AT VARIOUS DILUTIONS

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The quantity of heat developed by the neutralization of acids with bases has been the subject of numerous investigations. Hess,<sup>1</sup> Graham,<sup>2</sup> Andrews,<sup>3</sup> Favre and Silbermann,<sup>4</sup> Favre,<sup>5</sup> Thomsen,<sup>6</sup> Berthelot,<sup>7</sup> v. Steinwehr,<sup>8</sup> Wörmann,<sup>9</sup> Rümelin,<sup>10</sup> Mathews and Germann<sup>11</sup> and Muller<sup>12</sup> (among others) have made measurements of this kind, using many different methods and varying the conditions widely. The fact observed by the earlier experimenters that with strong acids and bases the heat liberated is almost (but not quite) independent of the base or acid used, found explanation when the theory of electrolytic dissociation was developed by Arrhenius.<sup>13</sup> As every chemist knows, the action is now considered as being essentially that between hydrogen and hydroxyl ions alone, the other ions remaining almost if not quite undisturbed in the process. The experimental results coincided approximately with this theory, but the data available at the time when this investigation was begun were

<sup>1</sup> Hess, *Pogg. Ann.*, **50**, 385 (1840); **53**, 499 (1841); **57**, 569 (1842).

<sup>2</sup> Graham, *Ann. chim. phys.*, [3] **13**, 188 (1845).

<sup>3</sup> Andrews, *Pogg. Ann.*, **54**, 208 (1841); **143**, 101 (1871).

<sup>4</sup> Favre and Silbermann, *Ann. chim. phys.*, [3] **37**, 494 (1853).

<sup>5</sup> Favre, *Compt. rend.*, **73**, 772 (1871).

<sup>6</sup> Thomsen, "Thermochemische Untersuchungen," Barth, vol. I, **1882**.

<sup>7</sup> Berthelot, "Thermochemie," Ganthier, vols. I and II, **1897**.

<sup>8</sup> v. Steinwehr, *Inaug. Diss.*, Göttingen, **1900**.

<sup>9</sup> Wörmann, *Ann. Physik*, [4] **18**, 775 (1905).

<sup>10</sup> Rümelin, *Inaug. Diss.*, Göttingen, **1905**.

<sup>11</sup> Mathews and Germann, *J. Phys. Chem.*, **15**, 73 (1911).

<sup>12</sup> Muller, *Bull. soc. chim.*, [4] **23**, 8 (1918).

<sup>13</sup> S. Arrhenius, *Z. physik. Chem.*, **1**, 631 (1887).

not adequate to determine whether the deviations between them were due to differences in the heats of dissociation of the remaining undissociated fractions of the several greatly ionized substances, or whether the differences were due merely to experimental inaccuracies. The thermal behavior of weak acids and bases is indubitably complicated by heats of dissociation.

In seeking an answer to the question, our first step was to determine with accuracy many heats of dilution of strong acids and alkalies, and their salts. The results were published in *THIS JOURNAL*, in 1920 and 1921.<sup>14</sup> Of course these heats of dilution (as will be exemplified later) fix the change of heat of neutralization with change of concentration. They were found to be so great, even at considerable dilution, as to influence the heats of neutralization to an important degree. This having been accomplished, the next step was to determine accurately, under precisely similar conditions, many heats of neutralization at one definite concentration, in order to provide a basis for the calculation of accurate values at all other concentrations, and especially to extrapolate the results to infinite dilution, when the heats of dilution would be zero (the idiosyncrasies of the individual salts having supposedly been eliminated) and the result should indicate the true heat of dissociation of water. The results of this part of the work follow. The research, which formed a part of the comprehensive thermochemical study of electrolytes,<sup>15</sup> was begun in 1907, and was continued, with occasional interruptions, for 7 years, the last experimental work recorded in the present paper having been done in June, 1914. Publication has been delayed by the war, and other preoccupations which postponed the time-consuming correlation and recalculation of the copious experimental material.

With the help of the adiabatic calorimeter<sup>16</sup> which has been used in this laboratory since 1905, we hoped to attain greater accuracy than had yet been possible. Serious possibilities of error in the earlier methods were soon discovered. The most important of these errors were found to be: first, defects in the methods of mixing the solutions, involving irregular cooling effects; and second, the presence of carbonate in the alkalies. The outcome leads to a considerably higher estimate of the heat of neutralization of the strong acids and bases than was formerly believed to exist. There is reason to hope that this conclusion is trustworthy, since the various checks and cross-verifications to which the work has been submitted have been satisfactory: the mass of data forms a reasonably

<sup>14</sup> Richards and Rowe, *THIS JOURNAL*, **42**, 1621 (1920); **43**, 770 (1921).

<sup>15</sup> Richards and Rowe, *Proc. Am. Acad.*, **43**, 473 (1908); *Z. physik. Chem.*, **64**, 187 (1908). Richards, Rowe and Burgess, *THIS JOURNAL*, **32**, 1176 (1910). Richards and Rowe, *Proc. Am. Acad.*, **49**, 173 (1913); *Z. physik. Chem.*, **84**, 585 (1913); *THIS JOURNAL*, **42**, 1621 (1920); **43**, 770 (1921).

<sup>16</sup> Richards, Henderson and Forbes, *Proc. Am. Acad.*, **41**, 1 (1905).

consistent whole. Furthermore, the suspicion that the old results were too low has been confirmed in a welcome manner as regards sodium chloride by an interesting result of F. G. Keyes<sup>17</sup> and his assistants, attained by a radically different method without knowledge of the quantitative outcome of our work and entirely independent of it.<sup>18</sup>

Because our work dealt with many substances at various temperatures and widely varying concentrations, a variety of interesting conclusions may be drawn from it which were not within reach before. These conclusions are explained in the latter part of this paper.

**Apparatus.**—The adiabatic calorimeter used in this research has been already described in full detail, having been employed for the heats of dilution of salt solutions with equal volumes of water.<sup>19</sup> It is pictured in the diagram on p. 1623, of *THIS JOURNAL*, vol. 42 (1920).

In brief, it consisted of an inner platinum can (a) of 0.7-liter capacity to contain the alkali, and an outer platinum can of double the capacity, A, to contain the acid in the annular space between the two cans. The inner can was provided with small stoppered baffled holes (g,g) below, and larger stoppered holes (k,k, and C) above and below; these holes could be opened one by one to effect gradual mixing. The stirrers (one in each can) were reciprocating: one rose when the other fell. Thus they exerted a backwards and forwards pumping effect on the liquid, through the holes in the inner can. Since one rose as the other fell, there was little or no tendency to draw in air from the outside, or to expel it. The stirring correction was negligible—and the precision of adjustment was proved by the perfect constancy of temperature before and after the reaction.

The whole was enclosed (with an intervening air space) in a water-tight burnished nickel-plated copper receptacle ("submarine") which was immersed in the outer bath. This outer bath was warmed during a determination at exactly the same rate as the calorimeter, the equality of temperature being established with the help of thermometers both in the inner can of the calorimeter and the annular space, as well as in the outside bath. It was shown that the mixing of acid and alkali progressed with great regularity. No difference of more than  $0.03^{\circ}$  between the liquid in the innermost can and that in the annular space between a and A ever appeared during the 10 minutes needed for complete neutralization. Hence it was possible to obtain very satisfactory adiabatic conditions; the great difficulty of irregular mixing had been overcome.

The apparatus was arranged in this form primarily in order that the two solutions should have exactly the same temperature at the moment of mixing. Many trials had convinced us of the difficulty of introducing a so-

<sup>17</sup> Keyes, Gillespie and Mitsukuri, *THIS JOURNAL*, 44, 707 (1922).

<sup>18</sup> Professor Keyes has kindly communicated to me orally the result of his most recent work, which essentially confirms our conclusion that the old values for heats of neutralization were much too low. For a description of the method as applied to dilution, see J. B. Dickson, *Thesis*, Mass. Inst. Technology, Boston, 1917. His value for sodium chloride is even somewhat higher than ours.

<sup>19</sup> Richards and Rowe, *THIS JOURNAL*, 42, 1622, 1625 (1920).

lution from outside the calorimeter without causing uncertainty as to the exact temperature of this added solution at that moment. Accordingly the two solutions were placed in concentric cans, and thus attained precisely uniform temperature before mixing. The form of apparatus prevented the mixing from being very rapid. This was not a disadvantage, since it enabled the adjustment of the adiabatic conditions to be made with much greater accuracy. Mathematically (according to the usual exponential expression, which, however, probably does not hold here with exactness), the increase of accuracy in this adjustment must be proportional to the increase in time, or the outcome will suffer. This condition was probably more than fulfilled.

The complete mixing of liquids is not always as prompt as it seems. The accurate quantitative analyst knows that he must shake his volumetric solutions very thoroughly in order to attain homogeneity. Thermal homogeneity is perhaps easier to attain than homogeneity of material, since thermal conduction assists in its attainment. In the present case, however, the equable distribution of the *substances* present is necessary, especially if they are present exactly in equivalent proportions. Our custom of al-

ways using a slight excess of alkali was a distinct help in this respect, since our neutralization was complete when the mixing process still lacked 0.5% of completeness. Some of the earlier experimenters on heat of neutralization doubtless lost sight of this danger; in their work the rise of temperature which ought to have been caused by the evolution of the last few calories was masked by the cooling effect, of which usually very inadequate account was taken. The adiabatic method affords the best method of detecting and avoiding this cause of error; it eliminates the cooling effect, and enables the slow conclusion of the mixing process to be followed thermometrically. The accurate study of

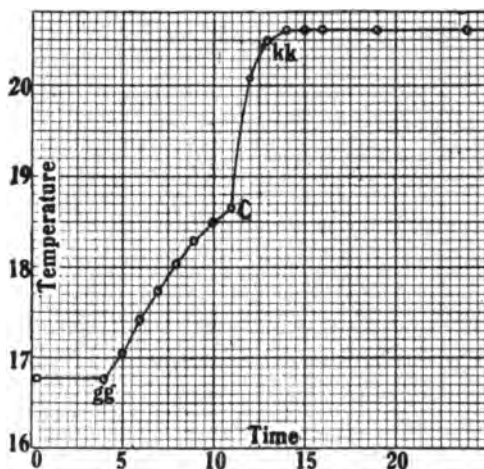


Fig. 1.—The course of a typical experiment. Temperatures are ordinates; times (in minutes), abscissas. After 4 minutes' test of constancy of temperature, the small orifices *g,g* were opened; after 7 minutes more, the central plug *C* was opened; 2 minutes later the side valves *k,k* were opened. The temperature remained exactly constant indefinitely after two minutes' further mixing. The correction for heat developed by stirring was negligibly small.



slow reactions is indeed the most important province of the method.

Some experimenters have found difficulty in keeping the outside bath at the same temperature as the calorimeter proper when using an adiabatic calorimeter of this type, but our own experience has been that this is easily accomplished unless the reaction is so rapid as to make the estimation of temperature exchange with the surroundings uncertain according to any method of experimentation. In the present case, as already stated, the rise of temperature was so gradual that there was no difficulty whatever in maintaining the outside bath within a few hundredths of a degree of the temperature of the calorimeter at all times. The most serious possible constant error with any method seems to be from the cooling effect caused by evaporation through the tubes communicating with the outside air. This is much diminished and in most cases rendered harmless by plugging these outlets with cotton wool throughout the experiment; with our apparatus the arrangement of the stirrers almost eliminated it.

The thermometers were standardized with great care.<sup>20</sup> Of course the specific heats of the various solutions were necessary in order to make possible the calculation of the results; their determination has already been described in full in earlier papers, the final results for the specific heats having been given in our paper of 1921.

**The Preparation of Materials.**—The importance of purity of materials was very soon discovered. The heat of neutralization of a carbonate is far less than that of an hydroxide. If the acid is in equivalent quantity, or in excess, of course, both carbonate and hydroxide are neutralized. Accordingly, we used always a slight excess of alkali and soon found that with ordinary caustic solutions, the greater the excess used the greater was the observed heat of neutralization. This was traced to carbonate. When a sufficiently liberal excess of alkali was used to eliminate the influence of carbonate—in other words to leave that substance undecomposed in solution—the results were concordant and ceased to indi-

<sup>20</sup> At the time of experimentation the thermochemical thermometers were standardized in an exceedingly thorough and scrupulous manner by comparison with the Paris standards, as represented by our two thermometers Baudin 15200 and 15276. Recently, these two latter thermometers have been repeatedly compared with the platinum standard by O. C. Bridgeman and one of us, (using a Leeds and Northrup platinum thermometer standardized by the U. S. Bureau of Standards) as well as very kindly by Professor H. N. Davis and V. Yngve (using the very accurate platinum thermometers of the Jefferson Physical Laboratory of Harvard University). The two entirely independent series of results with the platinum thermometers essentially agreed. The algebraic sum of the original correction referred to the Baudin thermometers and the supercorrection of the Baudin referred to the platinum standard was applied in each case. Hence, all the results given in this paper refer to the present standard of temperature as indicated by the contemporary platinum thermometer. For the short intervals used in the previous papers on heat of dilution, the Baudin thermometers were essentially correct according to this standard.

cate a larger figure with yet further excess of alkali. Thomsen used an excess of acid. Berthelot expresses his results in terms of alkali, a fact which suggests that he used an excess of acid, although his description apparently implies that exactly equivalent amounts were used. In either case, carbonate would affect the neutralization values. More recent workers may have used more precaution, but this point is not always made entirely clear; at any rate it is not emphasized. Keyes,<sup>17</sup> in his very recent work, quite independently has come to the same conclusion as that to which we came in 1909. There can be no doubt as to the deleterious effect of carbonate in most of the earlier work.

While it was possible to eliminate the effect of carbonate by the use of an adequate excess of alkali, this practice, if carried to an extreme, would cause uncertainty in the calculation of the final value, because of the effect of the excess on the heat capacity of the solution. For that reason, in our work each alkali was carefully freed from carbonate, as indicated below.

In the cases of sodium and potassium very pure inported solid hydroxide was dissolved in a quantity of pure freshly distilled water somewhat less than that needed for the desired concentration. Having been titrated for its carbonate content, this solution was treated with slightly more than the calculated amount of a hot saturated solution of barium hydroxide. After thorough mixing the solution was allowed to stand until the precipitated barium carbonate had completely settled. The clear supernatant liquid was then siphoned into a clean paraffin-lined bottle.<sup>21</sup> Several portions of this liquid were then drawn off, weighed, neutralized with pure hydrochloric acid and determined as to their barium content, gravimetrically through precipitation as sulfate. The exact amount of very pure sulfuric acid necessary to precipitate the barium present was added to the solution in the paraffin-lined bottle; and after thorough shaking and a sufficient lapse of time, fully protected from the air of the room, the liquid was again siphoned into another paraffin-lined bottle, titrated, diluted to the exact strength with water free from carbon dioxide, and finally analyzed with great care to determine its exact composition. It was protected by a safety tube containing caustic alkali.

The analysis was conducted with great care by means of weight burets, using

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<sup>21</sup> These bottles were of 8- to 20-liter capacity and after having been thoroughly cleaned and dried, were heated to about 80°, when about 0.7 liter of specially purified, melted paraffin was poured into each. With the glass stopper inserted, the bottle was slowly inverted and rotated so that concentric layers of the paraffin formed on the inner surface of the glass walls as the substance solidified. When the neck and shoulders of the bottle were thoroughly coated, the bottle, still constantly rotated, was brought to a horizontal position and the walls in turn were covered. Finally the bottle was restored to its normal position and the remaining paraffin allowed to solidify slowly at the bottom. The glass stopper was next withdrawn and the the paraffin coating across the neck excised with a sharp knife, and the edges of the still warm and plastic paraffin smoothed. The inside of the neck was painted with hot liquid paraffin and when this had cooled the glass stopper, heated to the melting point of the wax, was again inserted and rapidly rotated. The stopper was again withdrawn and the whole allowed to cool. Bottles prepared in this way have been used for over two years without the development of any break in the lining.

methyl red<sup>22</sup> as an indicator. The standard was hydrochloric acid, which was prepared in several solutions from time to time and analyzed gravimetrically by precipitation of the chlorine of silver chloride. The acid solutions were analyzed and used soon after preparation, since in time alkali dissolved from even the best glass diminishes slightly the hydrogen-ion concentration without affecting the chloride contents. The titer of the sodium hydroxide solution was proved to remain essentially constant even after having been in a paraffin bottle for over 7 months. The weight burets were of the familiar Ripper type.

Further details concerning the preparation of potassium and sodium hydroxides and of hydrochloric and nitric acids (which last had both been carefully redistilled with the usual precautions) are perhaps unnecessary, but the lithium hydroxide and the two other halogen acids need more detailed discussion. Because no lithium hydroxide of sufficiently pure quality was available in commerce, a quantity was prepared from a special sample of lithium chloride made for this research by the General Chemical Company, Baker and Adamson Works. This contained, according to factory analysis, less than 0.1% of the chlorides of sodium and potassium. Our own analysis (following the procedure recommended by Gooch<sup>23</sup> gave 0.0074 g. of the mixed chlorides in an 8g. sample—an excellent confirmation of the factory analysis. A kilogram of this salt was placed in a very large platinum dish and a small excess of a calculated amount of very pure sulfuric acid added. The mass was heated gradually and the excess of sulfuric acid slowly distilled, while the residue was occasionally stirred with a platinum spatula. The sulfate, found to be practically free from chloride, was weighed and dissolved in a minimum amount of water. A nearly saturated and carefully analyzed solution of very pure barium hydroxide was added in slight excess of the calculated amount to the lithium solution. After the large mass of barium sulfate had subsided, the clear supernatant liquid was siphoned, with the usual precautions against carbon dioxide, into a paraffin-lined bottle, and the excess of barium determined gravimetrically as sulfate. The calculated amount of sulfuric acid was then added to the main solution; and the clear liquid, after the separation of the resulting barium sulfate, was transferred (out of contact with the air of the room) to its final container, analyzed, properly diluted with freshly distilled water free from carbon dioxide, and finally analyzed once more to make certain that the true concentration had been attained. This solution, like the other alkaline solutions, was of course saturated with a trace of barium sulfate and paraffin, but each was harmless as regards our processes.

Hydrobromic acid was prepared by fractional distillation of a sufficiently pure specimen of the substance, likewise manufactured especially for this research. It contained no hydriodic acid and less than 0.1% of hydrochloric acid, which could have had no essential effect on the heat of neutralization, so that the preparation of a purer sample was considered to be unnecessary. Like all the other acids, it was suitably diluted and carefully analyzed by comparison with a known sodium hydroxide solution, standardized as described above.

Hydriodic acid offered difficulties absent in the case of other acids. The substance is unstable: iodine is set free by dissolved oxygen especially in the presence of light, and excess of alkali may thus form hypo-iodites of the several bases. These difficulties were not easy to overcome. Our initial material was concentrated acid especially prepared for this research by the manufacturers already mentioned. The factory analysis showed the amount of hydrochloric acid to be less than 0.03% while hydrobromic acid was absent. The solution contained a small amount of free iodine which imparted a yellow

<sup>22</sup> At the time of our earlier titrations, methyl red was not easy to obtain. We are indebted to Professor H. H. Willard for his kindness in furnishing the substance.

<sup>23</sup> Gooch, *Proc. Am. Acad.*, 22, 177 (1886).

color to the liquid. To this acid was added rather more pure distilled water than would dilute it to the constant boiling mixture and the resulting solution was fractionally distilled in the dark, using a quartz condenser and rejecting the initial portion of the distillate. The pure acid thus obtained was again fractionated under similar conditions and the final yellow distillate set aside for the work. Inasmuch as the oxygen dissolved in the diluent water is the factor determining the decomposition of the acid, water nearly free from this gas was prepared by bubbling very pure hydrogen through it for many hours. Weighed portions of the very pure conc. hydriodic acid were added to the water and, after a thorough shaking, more hydrogen was bubbled through the solution in the dark for another 2 hours. In drawing a sample, this first portion was always rejected together with enough of the unchanged solution to wash the tube thoroughly. The bottles, still kept in a dark cupboard, were connected through a suitable system of glass tubes and stopcocks with the delivery tube of the purifiers of the automatic hydrogen generator, and the withdrawal of acid samples was procured by the admission of the gas under pressure to the acid container. As is shown by the subsequent analyses, these precautions were quite adequate to protect the solutions from serious further decomposition. The small amount of free iodine originally present and still remaining was titrated by sodium thiosulfate, following the analytical procedure recommended by Treadwell.

In carrying out the initial analyses of the hydriodic acid solutions, the following routine was adopted. One of the weight burets was filled with the standard alkali while the other, carefully protected from the sunlight, contained the acid. A portion of acid was run into an Erlenmeyer flask in which had been placed about 0.1 liter of oxygen-free water. Inasmuch as the hydriodic acid was sufficiently concentrated to decompose somewhat the sodium thiosulfate solution, the major portion of the acid was neutralized. Neutral starch paste was added, and then exactly enough of the neutral thiosulfate solution to discharge the blue color of the iodine compound. The acid titration was completed in the usual manner, using methyl red. Preliminary controls showed that the hydrolysis of the sodium tetrathionate did not appreciably affect the end-point of the indicator. In all, three different samples of hydriodic acid were prepared and carefully analyzed.

The fact that the acid contained a little free iodine and that there was the possibility of further decomposition during a calorimetric experiment introduced several factors of uncertainty into the heat measurements. That the acid might decompose during a determination and thus lower the hydrogen-ion concentration was recognized and a procedure designed, as has already been stated, to eliminate error from this source. It was evident, however, that a simple iodine titration at the end of an experiment would not give the true iodine content of the reaction mixture, since some of the iodine would be attacked by the alkali always in excess. For this reason, the following method of analysis was adopted. At the end of a calorimetric determination the entire reaction-mixture was transferred to a large Erlenmeyer flask, starch paste added and thiosulfate solution run in until the blue color was discharged. This titration gave the free iodine remaining in the solution. The liquid was then slightly acidified with standard hydrochloric acid and the blue color again discharged by the addition of more thiosulfate. This gave the amount of iodine bound by the secondary reaction; and the sum of the two titrations gave the total iodine in the portion of acid used. From this, the total amount of free hydriodic acid which had actually been neutralized was readily computed.

The possible effect of the free iodine, however, did not cease here. The extraneous *thermal* effects from the decomposition of the acid during the actual calorimetric measurement and from the secondary hypo-iodite reaction had also to be considered. Fortunately, each of these effects was found to be negligible. By parallel experiments it was

found that only 2 mg. of iodine was set free during the 10 minutes needed for the thermo-chemical work, a quantity too small to affect the outcome appreciably.

The solutions used in the calorimetric work were all very close to a composition represented by the general formulas  $\text{MOH} \cdot 100 \text{ H}_2\text{O}$  and  $\text{HX} \cdot 100 \text{ H}_2\text{O}$ , almost always within  $0.2 \text{ H}_2\text{O}$ . The specific heats of these solutions were, therefore, within the limit of measurement, identical with those given in our previous paper<sup>24</sup> for  $100 \text{ H}_2\text{O}$  solutions. In making the calculations of the output of heat on a gram-molecular basis, however, the exact concentration of the acid solution, which was always used as a standard of reference, was taken into account, as will be seen in the sequel.

The following tables are typical of the grade of accuracy attained in these titrations, all of which were performed with weight burets.

TABLE I  
ACCURACY ATTAINED IN TITRATIONS  
Standardization of HCl reference solution

HCl ref. sol. G.	AgCl G.	HCl %
97.9121	9.4323	2.4507
101.9680	9.8233	2.4508
Standardization of $\text{NaOH} \cdot 100 \text{ H}_2\text{O}$ calorimetric solution		
HCl ref. sol. G.	NaOH cal. sol. G.	Mols $\text{H}_2\text{O}$ in NaOH sol.
45.31	56.19	100.205
48.09	59.60	100.183
50.01	62.01	100.190
52.78	65.43	100.168
Average		100.187

Successive tests of the  $\text{HCl} \cdot 100 \text{ H}_2\text{O}$  calorimetric solution by comparison with another alkali solution, again using the reference solution as a standard, gave successive values for its molal content of water as follows: 100.060; 100.060; 100.058; 100.077; in mean 100.063. Hence this solution had the formula  $\text{HCl} \cdot 100.06 \text{ H}_2\text{O}$ .

None of these weights was corrected to the vacuum standard, nor were the atmospheric conditions during weighing taken into account, unless these were very extreme, since the possible effects of both these corrections, especially the latter, were beyond the order of accuracy of the calorimetric part of the work. The vacuum correction, if applied, would diminish each final result by only about one part in 14,000 or about 1 calorie, since solid silver chloride was the standard of reference.

### The Calorimetric Determinations

With the apparatus and solutions prepared as described, careful calorimetric determinations were made of the heats of neutralization of each of the 4 acids with each of the 3 alkalies, giving 12 varieties of neutrali-

<sup>24</sup> Richards and Rowe, *THIS JOURNAL*, 43, 781, 782 (1921).

zation in all. Moreover, each process was conducted over two ranges of temperature, one finishing somewhat above and one somewhat below the temperature of  $20.00^{\circ}$ , in order to eliminate as much as possible unavoidable errors in the calibration of the thermometers. In a case like this where the heat capacities of the *factors* are used for the calculation of the result, the latter corresponds to an isothermal reaction conducted at the *final* temperature.<sup>25</sup> Each pair of results, therefore, was reduced to the value at exactly  $20.00^{\circ}$  by interpolation from the two values, one obtained above and one below the point desired. Another method of reducing all the results to  $20.00^{\circ}$  would have been to apply the temperature coefficients as determined in the previous paper to the results for the heat of neutralization at the two temperatures and take the average of the resulting figures. This method yields essentially the same result as the method adopted. The results at the higher and lower temperatures themselves could have been used for the calculation of the temperature coefficient of the reaction, but this seemed to us a questionable practice, since the temperature change (which rarely exceeded  $1.5^{\circ}$ ) was not large enough to give accurate values. The outcome (which averaged about  $-51$  cal. per degree) would represent a small difference between large quantities. Therefore the individual temperature coefficients calculated from these results could hardly be as accurate as the values (averaging also about  $-51$  cal.) calculated from the change of heat capacity in a previous paper.<sup>26</sup> The exact agreement of the average values is, however, strong confirmation of the accuracy of the combined corrections which had been applied to the thermometer scale.

The details of a single experiment, taken at random, may be given to elucidate the description (Table II).

The value thus obtained, namely, 13,853 calories ( $18^{\circ}$ ) represents the heat of the reaction  $\text{HCl.100 H}_2\text{O} + \text{NaOH.100 H}_2\text{O} = \text{NaCl.201 H}_2\text{O}$  at  $20.61^{\circ}$ . In order to make sure that the neutralization was complete and that there was an excess of ionized hydroxyl, the residual solution was titrated with acid. 1.08 cc. was needed to neutralize it, using phenolphthalein; and 0.40 cc. more was needed to attain the neutral point with methyl orange. Evidently, therefore, an ample, but not too great excess of sodium hydroxide had been present.

Table III contains the summarized results of all the 12 different neutralizations, each at two different temperatures. For the most part the conditions were essentially the same as those described for the detailed experiment. In three of the earlier determinations, (Nos. 8, 9, 10), 2 thermometers were present in the calorimeter in order to make sure of equable distribution of the increasing temperature. Hence in these

<sup>25</sup> Richards, *THIS JOURNAL*, 25, 209 (1903).

<sup>26</sup> Richards and Rowe, *ibid.*, 43, 795 (1921).

TABLE II  
THE NEUTRALIZATION OF NaOH.100 H<sub>2</sub>O BY HCl.100 H<sub>2</sub>O  
Series A, No. 4, Feb. 5, 1911 (Serial No. 11 in table below)

Heat capacity of the calorimetric system

	G.	Sp. heat	Heat capacity cal./t°
Platinum (cans, stirrers, wires, valves).....	455.29	0.0324	14.75
Rubber (valves).....	2.65	0.481	1.27
Thermometer II (portion immersed).....	.....	.....	2.48
Beeswax.....	0.23	0.62	0.14
Total heat capacity of apparatus (C')			18.64
HCl.100.06 H <sub>2</sub> O.....	610.29	0.9634	587.95
NaOH.100.19 H <sub>2</sub> O.....	615.31	0.9669	594.93
Total heat capacity			1201.52

Temperature change

Initial temperature (T <sub>1</sub> ) corrected.....	16.784°
Final temperature (T <sub>2</sub> ) corrected.....	20.612°
Difference (T <sub>2</sub> - T <sub>1</sub> ).....	3.828°
Corr. for stem temperature (24.0°).....	-0.002
T <sub>2</sub> - T <sub>1</sub>	3.826°

Heat evolved (Q) = 1201.52 × 3.826° = 4596.9 cal.

610.29 g. HCl.100.06 H<sub>2</sub>O solution = 0.33183 mol HCl

Therefore heat per mol acid =  $U = \frac{4596.9}{0.33183} = 13,853$  cal.

determinations the heat capacity of the apparatus was 20.13 units, instead of 18.64 units, which was the value in Serial Nos. 11 and 12. In all the other determinations the calorimeter was somewhat strengthened with extra platinum, but the second thermometer, having been found unnecessary, was omitted. In these cases (all except 8, 9, 10, 11, 12) the heat capacity of the apparatus was 18.98 units. The specific heats of the 7 solutions containing (per 100 mols of water) one mol each of KOH,<sup>27</sup> NaOH, LiOH, HCl, HBr, HI and HNO<sub>3</sub> had been found in earlier parts of the research, and were accordingly taken as 0.9567; 0.9669; 0.9813; 0.9634; 0.9433; 0.9213 and 0.9583, respectively.<sup>28</sup> As above, the 18° calorie is the heat unit indicated in the comprehensive table of data, since 18° was the mean temperature in both the specific heat and neutralization determinations. These values are afterwards expressed in terms of 20.00° calories and also of kilojoules. The atomic weights used are the current international values: H=1.008; O=16.00; K=39.10; Na=23.00; Li=6.94; Cl=35.46; Br=79.92; I=126.92; N=14.008.

<sup>27</sup> Attention is called to an unfortunate error in the specific heat of KOH.100 H<sub>2</sub>O in our previous paper (Ref. 24, p. 782). The molecular weight was wrongly taken as 1859.7 instead of 1857.7. Accordingly the specific heat was given as 0.9556 instead of the true value 0.9567. Compare *Proc. Am. Acad.*, 49 198 (1913).

<sup>28</sup> Ref. 15; see our papers, p. 198 (1913); p. 1632 (1920) and pp. 781, 782 (1921).

TABLE III

HEATS OF NEUTRALIZATION ( $U$ ) OF FOUR ACIDS BY THREE BASES

Each given at three temperatures in 18° calories

HYDROCHLORIC ACID						
Expt.	Weight of HCl sol. + 100.15 H <sub>2</sub> O	Weight of KOH sol.	Final tempera- ture ° C.	$T_2^\circ - T_1^\circ$ corrected ° C.	$U_{T^\circ}$	$U_{18^\circ}$
1	610.20	618.64	20.68	3.864	13,972	
2	610.25	618.68	20.61	3.865	13,976	
3	610.24	619.72	20.61	3.862	13,973	
Heat of neut. HCl.100 H <sub>2</sub> O + KOH.100 H <sub>2</sub> O at 20.63°					13,974	
4	610.34	619.62	19.47	3.876	14,026	
5	610.25	619.65	19.55	3.879	14,038	
6	610.28	619.69	19.41	3.877	14,031	
7	610.26	619.62	19.58	3.879	14,037	
Heat of neut. HCl.100 H <sub>2</sub> O + KOH.100 H <sub>2</sub> O at 19.50°					14,033	
Heat of neut. HCl.100 H <sub>2</sub> O + KOH.100 H <sub>2</sub> O at 20.00°						14,007
Expt.	Weight of HCl sol. + 100.06 H <sub>2</sub> O	Weight of NaOH sol.	Final tempera- ture ° C.	$T_2^\circ - T_1^\circ$ corrected ° C.	$U_{T^\circ}$	$U_{18^\circ}$
8	610.26	615.24	20.63	3.824	13,863	
9	610.24	615.29	20.61	3.822	13,855	
10	610.16	615.26	20.68	3.821	13,848	
11	610.29	615.31	20.61	3.826	13,853	
12	610.27	615.31	20.57	3.828	13,860	
Heat of neut. HCl.100 H <sub>2</sub> O + NaOH.100 H <sub>2</sub> O at 20.62°					13,856	
13	610.22	615.42	19.50	3.841	13,912	
14	610.24	615.44	19.55	3.841	13,912	
15	610.26	615.42	19.42	3.843	13,918	
16	610.24	615.42	19.56	3.844	13,915	
Heat of neut. HCl.100 H <sub>2</sub> O + NaOH.100 H <sub>2</sub> O at 19.50°					13,914	
Heat of neut. HCl.100 H <sub>2</sub> O + NaOH.100 H <sub>2</sub> O at 20.00°						13,888
Expt.	Weight of HCl + 100.00 H <sub>2</sub> O	Weight of LiOH sol.	Final tempera- ture ° C.	$T_2^\circ - T_1^\circ$ corrected ° C.	$U_{T^\circ}$	$U_{18^\circ}$
17	610.30	609.37	20.71	3.843	13,946	
18	610.28	609.37	20.75	3.844	13,949	
19	610.27	609.37	20.68	3.844	13,949	
Heat of neut. HCl.100 H <sub>2</sub> O + LiOH.100 H <sub>2</sub> O at 20.71°					13,948	
20	610.27	609.42	19.34	3.863	14,018	
21	610.29	609.39	19.33	3.864	14,022	
22	610.29	609.39	19.37	3.863	14,019	
Heat of neut. HCl.100 H <sub>2</sub> O + LiOH.100 H <sub>2</sub> O at 19.35°					14,020	
Heat of neut. HCl.100 H <sub>2</sub> O + LiOH.100 H <sub>2</sub> O at 20.00°						13,985



## HYDROBROMIC ACID

Expt.	Weight of HBr + 100.20 H <sub>2</sub> O	Weight of KOH sol.	Final tempera- ture ° C.	$T_2^\circ - T_1^\circ$ corrected ° C.	$U_T^\circ$	$U_{25}^\circ$
23	630.20	624.78	20.67	3.847	13,945	
24	630.20	624.78	20.73	3.848	13,949	
25	630.20	624.78	20.72	3.841	13,924	
26	630.20	624.78	20.74	3.846	13,942	
Heat of neut. HBr.100 H <sub>2</sub> O + KOH.100 H <sub>2</sub> O, at 20.72°					13,940	
27	630.20	624.68	19.39	3.867	14,016	
28	630.20	624.78	20.35	3.868	14,021	
29	630.20	624.78	20.38	3.866	14,015	
30	630.20	624.78	20.38	3.866	14,015	
Heat of neut. HBr.100 H <sub>2</sub> O + KOH.100 H <sub>2</sub> O at 19.38°					14,017	
Heat of neut. HBr.100 H <sub>2</sub> O + KOH.100 H <sub>2</sub> O at 20.00°						13,981
Expt.	Weight of HBr + 100.20 H <sub>2</sub> O	Weight of NaOH sol.	Final tempera- ture ° C.	$T_2^\circ - T_1^\circ$ corrected ° C.	$U_T^\circ$	$U_{25}^\circ$
31	630.20	618.35	20.66	3.810	13,813	
32	630.20	618.28	20.66	3.810	13,812	
33	630.20	618.35	20.64	3.807	13,802	
34	630.20	618.35	20.72	3.806	13,800	
Heat of neut. HBr.100 H <sub>2</sub> O + NaOH.100 H <sub>2</sub> O at 20.67°					13,807	
35	630.20	618.31	19.33	3.823	13,860	
36	630.20	618.28	19.34	3.826	13,871	
37	630.20	618.33	19.38	3.824	13,863	
38	630.20	618.33	19.36	3.825	13,867	
Heat of neut. HBr.100 H <sub>2</sub> O + NaOH.100 H <sub>2</sub> O at 19.35°					13,865	
Heat of neut. HBr.100 H <sub>2</sub> O + NaOH.100 H <sub>2</sub> O at 20.00°						13,836
Expt.	Weight of HBr + 100.24 H <sub>2</sub> O	Weight of LiOH sol.	Final tempera- ture ° C.	$T_2^\circ - T_1^\circ$ corrected ° C.	$U_T^\circ$	$U_{25}^\circ$
39	630.27	612.38	20.74	3.835	13,974	
40	630.28	612.39	20.70	3.833	13,967	
41	630.27	612.40	20.71	3.833	13,967	
42	630.27	612.27	20.67	3.833	13,967	
Heat of neut. HBr.100 H <sub>2</sub> O + LiOH.100 H <sub>2</sub> O at 20.71°					13,969	
43	630.28	612.40	19.36	3.849	14,026	
44	630.29	612.39	19.38	3.851	14,033	
45	630.28	612.39	19.40	3.852	14,036	
46	630.29	612.38	19.38	3.851	14,033	
Heat of neut. HBr.100 H <sub>2</sub> O + LiOH.100 H <sub>2</sub> O at 19.38°					14,032	
Heat of neut. HBr.100 H <sub>2</sub> O + LiOH.100 H <sub>2</sub> O at 20.00°						14,002

HYDRIODIC ACID<sup>a</sup>

Expt.	Weight of HI sol.	Weight of KOH sol.	Final temperature ° C.	$T_2^\circ - T_1^\circ$ corrected ° C.	$U_T^\circ$	$U_{25}^\circ$
47	640.30	627.39	20.49	3.821	13.886	

48	640.27	622.37	19.31	3.827	13,945	
49	640.32	637.41	19.30	3.776	13,935	
Heat of neut. KOH.100 H <sub>2</sub> O + HI.100 H <sub>2</sub> O at 19.30°					13,940	
Heat of neut. KOH.100 H <sub>2</sub> O + HI.100 H <sub>2</sub> O at 20.00°						13,908
Expt.	Weight of HI sol.	Weight of NaOH sol.	Final temperature °C.	T <sub>2</sub> ° - T <sub>1</sub> ° corrected °C.	U <sub>T</sub> °	U <sub>30</sub> °
50	640.32	619.42	20.66	3.788	13,742	
51	640.29	619.42	20.69	3.787	13,738	
Heat of neut. NaOH.100 H <sub>2</sub> O + HI.100 H <sub>2</sub> O at 20.67°					13,740	
52	640.29	619.41	19.35	3.810	13,806	
53	640.31	619.38	19.31	3.810	13,812	
54	640.27	619.42	19.35	3.809	13,801	
Heat of neut. NaOH.100 H <sub>2</sub> O + HI.100 H <sub>2</sub> O at 19.34°					13,806	
Heat of neut. NaOH.100 H <sub>2</sub> O + HI.100 H <sub>2</sub> O at 20.00°						13,773
Expt.	Weight of HI sol.	Weight of LiOH sol.	Final temperature °C.	T <sub>2</sub> ° - T <sub>1</sub> ° corrected °C.	U <sub>T</sub> °	U <sub>30</sub> °
55	640.30	607.40	20.72	3.834	13,884	
56	640.30	607.37	20.70	3.827	13,880	
Heat of neut. LiOH.100 H <sub>2</sub> O + HI.100 H <sub>2</sub> O at 20.71°					13,882	
57	640.30	607.40	19.44	3.844	13,941	
58	640.30	607.37	19.45	3.846	13,949	
59	640.30	607.37	19.45	3.845	13,946	
Heat of neut. LiOH.100 H <sub>2</sub> O + HI.100 H <sub>2</sub> O at 19.45°					13,945	
Heat of neut. LiOH.100 H <sub>2</sub> O + HI.100 H <sub>2</sub> O at 20.00°						13,918

\* In each of these individual determinations the amount of hydriodic acid actually neutralized was carefully determined in the way already described. The individual amounts of HI in determinations Nos. 47 to 59 inclusive were, respectively, 42.563, 42.283; 42.250; 42.583; 42.582; 42.634; 42.613; 42.634; 42.565; 42.568; 42.570; 42.568 and 42.565 g. The full details of these laborious determinations would take too much space here, but the several quantities must be used in the calculation of *U*.

## NITRIC ACID

Expt.	Weight of HNO <sub>3</sub> + 100.19 H <sub>2</sub> O	Weight of KOH sol.	Final temperature °C.	T <sub>2</sub> ° - T <sub>1</sub> ° corrected °C.	U <sub>T</sub> °	U <sub>30</sub> °
60	620.24	620.65	20.62	3.862	14,040	
61	620.27	620.62	20.66	3.863	14,043	
62	620.25	620.63	20.61	3.862	14,038	
Heat of neut. KOH.100 H <sub>2</sub> O + HNO <sub>3</sub> .100 H <sub>2</sub> O at 20.63°					14,040	
63	620.24	620.17	19.47	3.885	14,119	
64	620.24	620.65	19.49	3.876	14,091	
65	620.24	620.64	19.49	3.880	14,106	
66	620.24	620.62	19.50	3.880	14,106	
67	620.27	620.64	19.57	3.882	14,112	
68	620.25	620.64	19.55	3.884	14,120	
Heat of neut. KOH.100 H <sub>2</sub> O + HNO <sub>3</sub> .100 H <sub>2</sub> O at 19.52°					14,109	
Heat of neut. KOH.100 H <sub>2</sub> O + HNO <sub>3</sub> .100 H <sub>2</sub> O at 20.00°						14,079

Expt.	Weight of $\text{HNO}_3 +$ 100.17 $\text{H}_2\text{O}$	Weight of NaOH sol.	Final temperature ° C.	$T_2^\circ - T_1^\circ$ corrected ° C.	$U_{T^\circ}$	$U_{20^\circ}$
69	620.25	614.62	20.64	3.795	13,800	
70	620.25	614.62	20.55	3.796	13,803	
71	620.27	614.65	20.48	3.798	13,810	
72	615.24	614.67	20.55	3.778	13,795	
Heat of neut. $\text{NaOH} \cdot 100 \text{H}_2\text{O} + \text{HNO}_3 \cdot 100 \text{H}_2\text{O}$ at 20.55°					13,802	
73	620.26	614.58	19.29	3.810	13,855	
74	620.18	614.69	19.43	3.809	13,853	
75	620.27	614.68	19.33	3.813	13,866	
76	620.24	614.62	19.38	3.811	13,858	
77	620.27	614.62	19.32	3.815	13,873	
78	620.25	614.67	19.37	3.812	13,862	
79	620.25	614.67	19.47	3.813	13,865	
Heat of neut. of $\text{NaOH} \cdot 100 \text{H}_2\text{O} + \text{HNO}_3 \cdot 100 \text{H}_2\text{O}$ at 19.37°					13,862	
Heat of neut. of $\text{NaOH} \cdot 100 \text{H}_2\text{O} + \text{HNO}_3 \cdot 100 \text{H}_2\text{O}$ at 20.00°						13,830
Expt.	Weight of $\text{HNO}_3 +$ 100.19 $\text{H}_2\text{O}$	Weight of LiOH sol.	Final temperature ° C.	$T_2^\circ - T_1^\circ$ corrected ° C.	$U_{T^\circ}$	$U_{20^\circ}$
80	620.27	610.37	20.68	3.786	13,823	
81	620.27	610.35	20.66	3.786	13,823	
82	620.29	610.40	20.72	3.787	13,826	
83	620.32 <sup>a</sup>	611.85	20.68	3.785	13,824	
84	620.32 <sup>a</sup>	611.82	20.68	3.785	13,824	
Heat of neut. $\text{LiOH} \cdot 100 \text{H}_2\text{O} + \text{HNO}_3 \cdot 100 \text{H}_2\text{O}$ at 20.690°					13,824	
85	620.27	610.37	19.31	3.804	13,887	
86	620.29	610.37	19.29	3.805	13,891	
87	620.29	610.39	19.29	3.805	13,891	
88	620.29 <sup>a</sup>	615.37	19.33	3.797	13,891	
89	620.30 <sup>a</sup>	611.82	19.33	3.804	13,893	
Heat of neut. $\text{LiOH} \cdot 100 \text{H}_2\text{O} + \text{HNO}_3 \cdot 100 \text{H}_2\text{O}$ at 19.30°					13,890	
Heat of neut. $\text{LiOH} \cdot 100 \text{H}_2\text{O} + \text{HNO}_3 \cdot 100 \text{H}_2\text{O}$ at 20.00°						13,856

<sup>a</sup> These four determinations were made subsequently to the others with entirely new solutions. The new nitric acid solution was of the composition  $\text{HNO}_3 \cdot 100.09 \text{H}_2\text{O}$ , a circumstance which must be taken into account in calculating these four determinations.

After the conclusion of these systematic determinations, which took many months, a single confirmatory calorimetric determination was made with each pair of solutions (excepting those pairs including potassium hydroxide, of which all our pure material had been exhausted). In some cases fresh solutions were prepared and analyzed; in others new analyses were made of solutions used before. The confirmation was on the whole very good, the maximum deviation of a single determination from the appropriate average given above being less than 0.07%, and the mean deviation being only 0.04%. These check determinations were made at various temperatures in the neighborhood of 20.00°; of course, the

temperature coefficient of the reaction was duly reckoned into this calculation. The satisfactory agreement of these "control" determinations tends to show that no serious accidental error could have entered into the work. Even if some unsuspected *constant* error should have been present, it must have affected all the results alike, and hence be without effect on the comparison of the several values.

This being the case, it is a matter of great interest to compare the results with one another, and of still greater interest to compare them with values of heats of neutralization at other concentrations. First, the values may be tabulated as follows (each augmented by 0.05% in order to convert it to terms of the 20.00° calorie, and also reduced to kilojoules) in parallel columns (1 cal. (20.00°) = 0.004180 kj.).

TABLE IV  
VALUES OF  $U_{20^\circ}$  OF NEUTRALIZATION YIELDING MX.201 H<sub>2</sub>O  
In 20° calories and kilojoules

	KOH		NaOH		LiOH	
	Cal.	Kj.	Cal.	Kj.	Cal.	Kj.
HCl.....	14,014	58.58	13,895	58.08	13,993	58.49
HBr.....	13,988	58.47	13,843	57.86	14,009	58.56
HI.....	13,915	58.16	13,780	57.60	13,925	58.21
HNO <sub>3</sub> .....	14,086	58.87	13,837	57.83	13,863	57.94

The values thus arranged show some systematic tendency: in particular, those for potassium salts are always greater than those for sodium salts, and those for bromides always greater than those for iodides. Nevertheless in other cases they exhibit distinct irregularity.

For the sake of completeness the temperature coefficients of six of these heats of neutralization are given below, having been calculated from the heat capacities of factors and products in our previous paper (p. 795). The necessary data for the other six have not yet been determined, but will be studied in the near future.

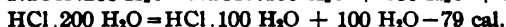
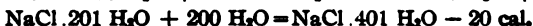
TABLE V  
TEMPERATURE COEFFICIENTS OF HEATS OF NEUTRALIZATION  
In calories and kilojoules per 1°

	G. calorie units		Kilojoule units	
	HCl.100 H <sub>2</sub> O	HNO <sub>3</sub> .100 H <sub>2</sub> O	HCl.100 H <sub>2</sub> O	HNO <sub>3</sub> .100 H <sub>2</sub> O
LiOH (100 H <sub>2</sub> O).....	-55.4	-53.6	-0.232	-0.224
NaOH (100 H <sub>2</sub> O).....	-52.7	-50.5	-0.220	-0.211
KOH (100 H <sub>2</sub> O).....	-48.4	-45.1	-0.202	-0.189
Av.....	-52.1	-49.7	-0.218	-0.209

Most properties of solutions tend toward greater regularity with increasing dilution. Therefore, it is desirable to discover the change in heat of neutralization with increasing volume; this was indeed one of the chief objects of the research. The calorimetric work of others was not suffi-

ciently precise to form the basis of any certain conclusions with regard to the question. Our data, however, furnish exactly the best means of securing the desired values. For example, the heat of the reaction  $\text{NaOH} \cdot 200 \text{ H}_2\text{O} + \text{HCl} \cdot 200 \text{ H}_2\text{O} = \text{NaCl} \cdot 401 \text{ H}_2\text{O}$  may be obtained from the data concerning more concentrated solutions by simply taking account of the heats of dilution of factors and products, without performing anew the actual experimental calorimetric neutralization of the dilute solutions. The needed heats of dilution are implied in the figures recorded in our next previous publication.<sup>29</sup> Each value needed for this particular case may be obtained very simply by subtraction of two figures there given; e. g., in the case of sodium hydroxide, the value  $-127$  given for the reaction  $\text{NaOH} \cdot 10 \text{ H}_2\text{O} + 90 \text{ H}_2\text{O}$  is subtracted from the value  $-156$  given for the reaction  $\text{NaOH} \cdot 10 \text{ H}_2\text{O} + 190 \text{ H}_2\text{O}$ .<sup>30</sup> The difference ( $-29$  cal.) is the heat of dilution of  $\text{NaOH} \cdot 100 \text{ H}_2\text{O}$  to  $\text{NaOH} \cdot 200 \text{ H}_2\text{O}$ .

Applying the values thus calculated to the case in hand (transposing the dilution equations of the factors) we obtain the following typical thermochemical calculation, which gives the desired heat of neutralization in the more dilute solution.



Therefore

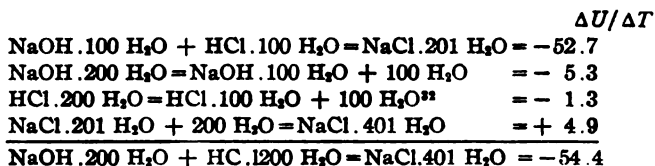


This result was satisfactorily confirmed by a series of direct neutralization experiments with the above named dilute solutions, carrying out calorimetrically the reaction  $\text{NaOH} \cdot 200 \text{ H}_2\text{O} + \text{HCl} \cdot 200 \text{ H}_2\text{O} = \text{NaCl} \cdot 401 \text{ H}_2\text{O}$ . These experiments were made, indeed, before the determination of the heat of dilution of the salt solution had made the above calculation possible. Ten determinations of this kind were made; the final temperatures (varying from  $17.44^\circ$  to  $20.65^\circ$ ) averaged  $18.89^\circ$ , and the average rise of temperature was about  $1.9^\circ$ . Naturally the agreement between

<sup>29</sup> Ref. 24, pp. 779, 780. It should be noted that the heat of dilution of  $\text{NaCl} \cdot 201 \text{ H}_2\text{O}$  to  $\text{NaCl} \cdot 401 \text{ H}_2\text{O}$  is  $0.3$  cal. different from that of  $\text{NaCl} \cdot 200 \text{ H}_2\text{O}$  to  $\text{NaCl} \cdot 400 \text{ H}_2\text{O}$ , as found from the curves giving heats of dilution at various concentrations. Even with double these concentrations the added molecule of water also makes less than  $1$  cal. difference. Only in the case of potassium nitrate is the correction important ( $4$  cal.) with this concentration. On diluting salt solutions containing as little as  $50 \text{ H}_2\text{O}$  the extra molecule has a more important effect, amounting to the following quantities:  $\text{KCl}$ ,  $3$  cal.;  $\text{KNO}_3$ ,  $13$  cal.;  $\text{NaCl}$ ,  $6$  cal.;  $\text{NaNO}_3$ ,  $8$  cal.;  $\text{LiCl}$ ,  $3$  cal.;  $\text{LiNO}_3$ ,  $0.6$  cal. All these corrections are applied in the table following. The sign of each correction is obvious; in each case it *diminishes* the thermal effect.

<sup>30</sup> These values are more trustworthy than those from  $\text{NaOH} \cdot 5.77 \text{ H}_2\text{O}$ , since these latter were the first dilution experiments carried out, and were less satisfactory in many ways than the later experiments.

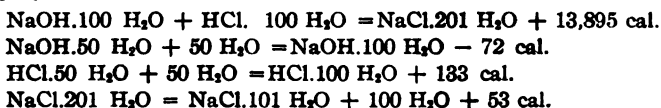
the successive results was less satisfactory than with the more concentrated solutions; the values ranged between 0.15% above to 0.15% below the mean, after correcting each value to the same temperature, and the "probable error" of the average result (13,879 cal. 18°) was about 3 cal. This evolution of heat corresponds to the isothermal reaction at 18.89°; and we need that at 20.00°. The temperature coefficient of the reaction may be found as usual from the difference of the heat capacities of factors and products on dilution<sup>21</sup> as follows (the signs in the second and third equations below being changed, because they apply in the reverse direction).



The decimals of these figures can hardly be certain, but the outcome is exact enough to show that the temperature coefficient of the dilute neutralization is not far from -54.4 cal./° C. The value 13,879 cal. at 18.89° then becomes 13,819 cal.<sub>18°</sub> when corrected to 20.00°, or 13,826 cal.<sub>20°</sub>.

The agreement of this result, 13,826, with that calculated in the more satisfactory way from the data for more concentrated solutions, with the help of dilution-heats, namely, 13,825, must be partly accidental, since it is much within the limit of error for the quantities concerned. Evidently the "control" thus afforded as to the data for all of the properties involved is entirely satisfactory.

The method of calculation from dilution-heats, being far more convenient and probably more exact than the direct determination in very dilute solutions, was used in calculating also the heats of neutralization of the five other processes for which data were available. Not only the values for the more dilute solutions were thus obtained; the values of the heats of neutralization for more concentrated solutions were calculated in a similar fashion. For example, to compute the heats of the reaction  $\text{HCl}.50 \text{ H}_2\text{O} + \text{NaOH}.50 \text{ H}_2\text{O} = \text{NaCl}.101 \text{ H}_2\text{O}$  the following equations are employed.



Therefore



<sup>21</sup> Ref. 24, pp. 779, 780, 795.

<sup>22</sup> Taken from the curve in our paper of 1920 on p. 1634.

In the same way the reaction  $\text{NaOH} \cdot 25 \text{H}_2\text{O} + \text{HCl} \cdot 25 \text{H}_2\text{O}$  was found to give 14,227 cal.

For the stage of dilution involving factors containing 400 mols of water, it was needful to obtain the corresponding values of heats of dilution of the products (to 0.0695 *N*, containing 801  $\text{H}_2\text{O}$ ) by slight extrapolation from the experimental results. This was done on a large scale with great care; curves were drawn like those in the next previous paper, using calories instead of kilojoules.<sup>22</sup> Thus the heats of dilution of the several salt solutions from 201 to 801 mols of water were found to be as follows:  $\text{KCl}$ , -26;  $\text{KNO}_3$ , -218;  $\text{NaCl}$ , -31;  $\text{NaNO}_3$ , -112;  $\text{LiCl}$ , +62;  $\text{LiNO}_3$ , +43 cal. These values were combined as before with the appropriate values found directly for the alkalis and acids (diluted from 100 to 400 mols of water) to calculate the heats of neutralization of these very dilute solutions. The experimental errors are greatly magnified in the calculation, therefore the results are necessarily less trustworthy than those with greater concentrations; but at least they present the best information now available concerning the questions chiefly at issue.

The results thus found are recorded in the following double table which records all the values first in 20° calories and again in kilojoules.

HEATS OF NEUTRALIZATION AT VARIOUS CONCENTRATIONS  
In 20° calories (temperature 20°)

Mols $\text{H}_2\text{O}$ In factors = In products = Reaction	25 + 25 51	50 + 50 101	100 + 100 201	200 + 200 201	400 + 400 801	Extra- polated (Parabolic) Infinite
$\text{KOH} + \text{HCl}$	14,569	14,209	14,014	13,905	13,819	13,695
$\text{KOH} + \text{HNO}_3$	14,724	14,325	14,086	13,934	13,834	13,700
$\text{NaOH} + \text{HCl}$	14,228	14,009	13,895	13,825	13,761	13,660
$\text{NaOH} + \text{HNO}_3$	14,012	13,892	13,837	13,790	13,756	13,705
$\text{LiOH} + \text{HCl}$	14,433	14,149	13,993	13,889	13,803	13,685
$\text{LiOH} + \text{HNO}_3$	13,986	13,905	13,863	13,825	13,788	13,715
					Average	13,693
In kilojoules (temperature 20°) (1 kilojoule = 4,180 calories (20°))						
$\text{KOH} + \text{HCl}$	60.90	59.39	58.58	58.12	57.76	57.25
$\text{KOH} + \text{HNO}_3$	61.55	59.88	58.88	58.24	57.83	57.27
$\text{NaOH} + \text{HCl}$	59.47	58.56	58.08	57.79	57.52	57.10
$\text{NaOH} + \text{HNO}_3$	58.57	58.07	57.84	57.64	57.50	57.29
$\text{LiOH} + \text{HCl}$	60.33	59.14	58.49	58.06	57.70	57.20
$\text{LiOH} + \text{HNO}_3$	58.46	58.12	57.95	57.79	57.63	57.33
					Average	57.24

All the figures (excepting the last column) in the upper half of this

<sup>22</sup> See Ref. 24, p. 786.

table were plotted with care. Smooth curves were then drawn by means of a device similar in principle to the curve ruler of Lord Berkeley.<sup>24</sup> The result, of which the more important part is depicted in Fig. 2, is striking. The curves, which are nearly straight lines with concentrated solutions, converge with increasing dilution, apparently tending almost toward a

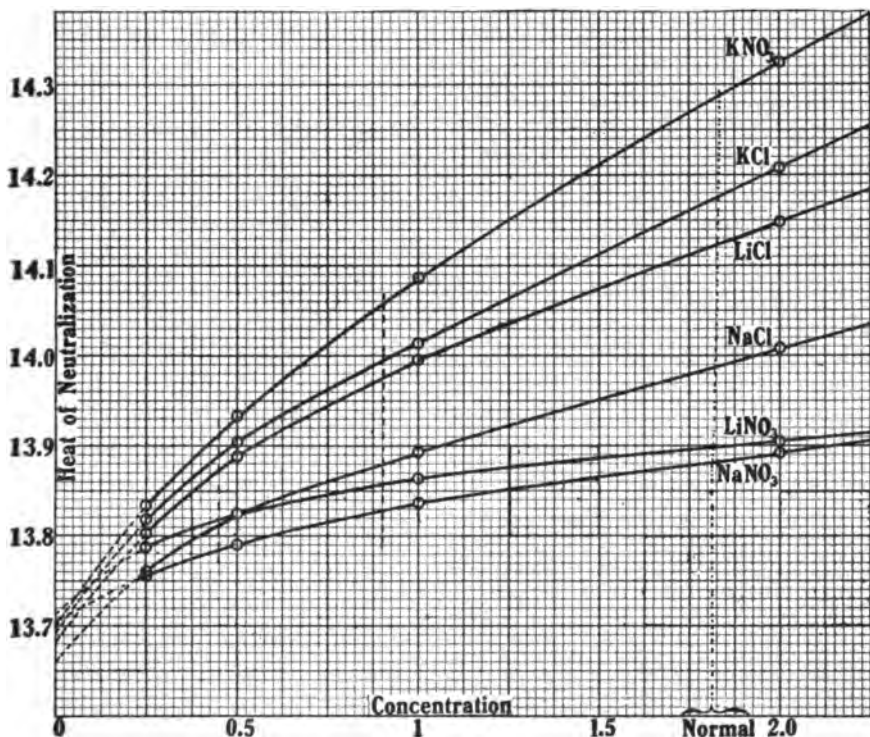


Fig. 2.—Heats of neutralization (at 20°) of all concentrations up to 50 H<sub>2</sub>O per mol of acid or alkali, for 3 bases and 2 acids. Kilogram calories are plotted as ordinates; concentrations in mols acid or alkali per 100 H<sub>2</sub>O of initial solutions are plotted as abscissas. *N*, 0.5*N* and 0.25*N* solutions are approximately indicated by broken vertical lines. The extrapolation is parabolic, based upon the left hand known portions of the curves as drawn with a flexible ruler under suitable unequal stresses.

single point. This point should give the heat of the reaction  $\text{H}^+ + \text{OH}^- = \text{H}_2\text{O}$ . Accordingly, the extrapolation of these curves is a matter of interest. Trial showed that the ruler had given their left hand branches a near-parabolic shape, although the right hand extremities are almost linear. Accordingly, at first parabolic equations were used for extrapolating to infinite dilution in order to obtain a maximum value (see below). For example, the parabola corresponding to potassium nitrate

<sup>24</sup> Lord Berkeley, *Phil. Mag.*, **24**, 664 (1912); Richards and Sameshima; *THIS JOURNAL*, **42**, 51 (1920).



had its focus at the point (outside the diagram)  $x = 0.348$  and  $y = 13.446$  with the parameter 0.87 cal. This fits all four known points on the diagram. Similar equations with decreasing parameters were found for the other curves, and with their help all the curves were extrapolated to infinite dilution. The values thus found are recorded in the last column of the foregoing table. The average, 13.69 Cal., may be supposed to be a maximum value for the heat of ionization of water, since the order of the curves can hardly be less than quadratic.

The nearly linear character of the right hand ends of the curves suggests the hyperbola; and this conic section also was tested. An hyperbola in which  $C = 1.065$ , and the latus rectum = 0.65, with focus at point  $x = 0.325$  and  $y = 13.54$  corresponds well with all the points in the potassium nitrate curve, even with the heat of neutralization of the most concentrated solution. This hyperbola cuts the  $y$  axis at the point 13.67—somewhat below the point given by the parabola. The nearest hyperbolas to the other curves also cut the  $y$  axis at lower points than the parabolas, but the agreement of these calculated curves with observed points, as well as the agreement between the resulting extrapolated values, is not much better than in the case of the parabolas.

According to either method the extrapolated values are not very concordant, the extremes differing by nearly 0.4%. This difference is

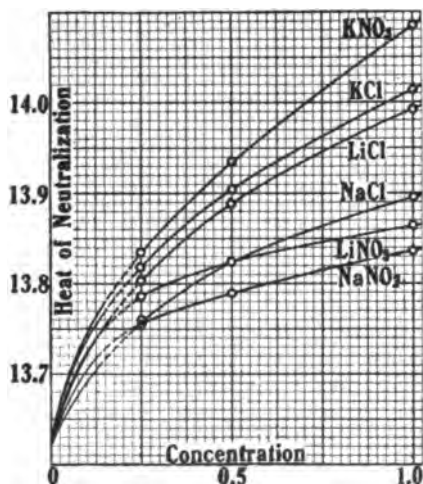


Fig. 3.—Heats of neutralization. Extrapolated, assuming exact convergence, to a compromise point.

not larger than many other thermochemical discrepancies, but it is worthy of consideration, since although many data are involved in each number, even the sum of possibly accumulated experimental inaccuracies could hardly explain the difference between the values for sodium chloride and lithium nitrate. Extrapolation of curves which, like these, are the result of the superposition of many individually undetermined tendencies, is an uncertain procedure. Probably the assumption of parabolic curvature is unwarranted; it certainly does not apply to the left hand branches of the curves. For other alternatives (including the logarithmic, and equations of higher powers) space is lacking. An entirely different mode of attacking the problem is to assume that the curves must come together at infinite dilution, and find a point

which seems to accomplish their convergence smoothly. Such a point could hardly correspond to more than 13,620 calories (on account of the shape of the sodium chloride curve) and might correspond to less. A small diagram (Fig. 3) repeats the neighboring known portions of the curves, and depicts this alternative assumption. On the whole this treatment of the results seems more reasonable than the other. When thus extrapolated, the curves show qualitative likeness to the well-known curves recording electrolytic conductivity. That heats of dilution (upon which these curves depend) give a verdict not very different from that of conductivity has been already pointed out.<sup>35</sup>

The final answer to the interesting questions thus raised must await further experimental investigation, involving also other salts, and yet greater dilution. This will be undertaken here in the near future.

The diagram (Fig. 2) is a convenient table of reference; it possesses no greater probable error than the results themselves. The heat of neutralization for any dilution of acid and alkali less than 1.25 *N* may obviously be read off directly from the graph, provided that the acid and alkali both have the same concentration. If their concentration is different, the appropriate heats of dilution must be duly entered in the reckoning. For convenience, normal, half normal, and quarter normal concentrations are marked approximately on the diagram.<sup>36</sup>

The previous published results of others, insofar as they may be compared with these, are usually much lower.<sup>37</sup> The most detailed of the earlier work seems to have been done by Wörmann, but his outcome differs from ours in many respects. There are really no results available in the literature which satisfactorily cover the ground of the present ones. Very few experimenters have given data suitable for even a rough extrapolation to infinite dilution.

<sup>35</sup> Ref. 24, p. 793.

<sup>36</sup> Normal solutions of potassium and sodium hydroxides, and hydrochloric and nitric acids (at 18°) have respectively the formulas KOH.55.1 H<sub>2</sub>O; NaOH.55.6 H<sub>2</sub>O; HCl.54.4 H<sub>2</sub>O; HNO<sub>3</sub>.53.8 H<sub>2</sub>O, calculated from the well-known densities of these solutions. That is to say, for each 100 mols of water there are present 1.815, 1.799, 1.838 and 1.859 mols of these substances, respectively. The average concentrations, thus given, of each neutralizing pair of these solutions fix the course of the slightly irregular nearly vertical dotted line in Fig. 2 which indicates closely the heat of neutralization of normal solutions. (Of course, to be absolutely exact, heats of dilution should be considered in fixing the points; but the solutions are so nearly equally hydrated that this precaution would be supererogatory with the present data.) Half normal and quarter normal loci are also noted. In a similar way, the heats of dilution of normal solutions can easily be found from the appropriate curves given in the previous paper. (Ref. 24, p. 786.)

<sup>37</sup> The following table giving values for NaOH + HCl will serve as an example of the comparison; the first column of figures gives the heat of neutralization as recorded by the observers; the second column, the average final temperature of the determination; the

The greater values with greater concentrations are, of course, dependent upon the varying heats of dilution of the several factors and products. These are specific properties of the individual compounds. In such a case as potassium nitrate, the effect of the salt is very great. The interesting specific curves of the several substances recorded in this paper tempt yet further discussion; they are bound to assist in the final interpretation of the nature of electrolytic solutions. For the present, however, this discussion may be postponed. Evidently the new results do not especially favor the recent theory that strong electrolytes are wholly dissociated in moderately concentrated solutions. As already stated, one of us hopes to continue the experimental investigation of the problem, with other substances and greater dilutions.

In conclusion, the authors take pleasure in expressing their indebted- last column, each heat of neutralization reduced to 20.00° by the temperature coefficient found by the observer in question.

Observer	$U$	$T_2$	$U_{20^\circ}$	Concentration
Richards and Rowe.....	13895	20.00	13895	HCl <sub>2</sub> .100 H <sub>2</sub> O, etc.
Thomsen.....	13627	24.60	13814	HCl <sub>2</sub> .100 H <sub>2</sub> O, etc.
	14247	10.14		

[*"Thermochemische Untersuchungen,"* I, pp. 63, 64 (1882)]

Berthelot.....	13690	?	13690 (?)	
v. Steinwehr.....	14085	11.80	13630 (?)	Very dilute solution
Wörmann.....	13731	19.86	13723	0.5 <i>N</i>
	13739	18.45	13658	0.25 <i>N</i>
	13703	17.08	13551	0.1 <i>N</i>
Rümelin.....	14100	11.40	13630 (?)	Very dilute solution
Richards and Rowe.....	13880	20.00	13880	0.5 <i>N</i>

Thomsen's first results were obtained in a roundabout way involving the neutralization of sulfuric acid and precipitation of barium sulfate. His later results are better in every respect, but his temperature coefficient is too low, for some unexplained reason. Wörmann's results are the most complete and systematic. He seems to have missed the effect of concentration with moderately dilute solutions, because he calculated his results for the mean temperature and not for the final temperature of the reaction, apparently using the heat capacities of the factors in his calculation. His temperature coefficients average nearly the same as ours, given in the previous paper. His results for potassium salts were much higher than those for sodium salts, although still lower than ours when correction is made to the same temperature. Probably his potassium hydroxide was purer than his sodium hydroxide. The work of J. A. Muller [*Bull. soc. chim.*, [4] 23, 8 (1918)], on potassium chloride and sulfate is very briefly stated. He extrapolated to infinite dilution but his method of extrapolation is not wholly clear. If the heat of dilution of the acids needs to be applied, that of the salt solutions also should be considered. As usual, heed is not given to the fact that when the heat capacities of the factors are used, the result corresponds to the final temperature. Muller's results, as stated, are therefore not comparable with ours. The interesting result of A. A. Noyes, Y. Kato and R. B. Sosman [*THIS JOURNAL*, 32, 159 (1910)], 13956 at 20°, was calculated rather indirectly from the hydrolysis of ammonium acetate. It agrees much better with our result than with earlier ones and is perhaps as near as could be expected under the circumstances.

ness to the Carnegie Institution of Washington, which through generous subsidy alone made possible the execution of this costly research.

### Summary

The results of this investigation may be summarized as follows.

1. The most serious errors in work of this kind were shown to be irregularity of mixing and presence of carbonate in the hydroxides, besides, of course, inadequate avoidance of loss of heat by cooling.

2. Solutions of uniform molal concentration (+ 100 H<sub>2</sub>O) of nitric and the three halogen acids and of three alkaline hydroxides have been mutually neutralized calorimetrically in all possible pairs over two ranges of temperatures not far apart, and the results interpolated exactly to 20°. The values ranged from 13,750 to 14,085, sodium hydroxide giving the lowest values among the bases, and hydriodic acid among the acids.

3. Check determinations based upon different analyses and performed independently at various temperatures showed complete agreement with the values originally obtained.

4. With the help of the heats of dilution of factors and products, previously determined, the heats of neutralization at other concentrations have been determined, and these have been extrapolated in two ways through a short range to infinite dilution.

5. The heat of formation of water from its ions at 20° is found by this short extrapolation to be probably not over 13.69 Cal.<sub>20°</sub> or 57.22 kilojoules, and possibly not under 13.62 Cal. or 56.93 kilojoules.

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[CONTRIBUTION FROM THE RESEARCH LABORATORY OF PHYSICAL CHEMISTRY OF THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY, No. 142]

## A CONTINUOUS-FLOW CALORIMETER, AND THE DETERMINATION OF THE HEAT OF NEUTRALIZATION OF A SOLUTION OF HYDROCHLORIC ACID BY ONE OF SODIUM HYDROXIDE

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The continuous-flow principle of calorimetry, which was developed by Callendar and Barnes<sup>1</sup> for measuring the specific heat of water, and applied by Swann<sup>2</sup> and by Scheel and Heuse<sup>3</sup> for specific heats of gases, offers certain advantages over the more usual calorimetry for heats of neutralization, dilution, etc. Among these advantages are equal adaptability to any temperatures at which thermostats can be successfully

<sup>1</sup> Callendar and Barnes, *Trans. Roy. Soc. (London)*, **199A**, 55-263 (1902).

<sup>2</sup> Swann, *Proc. Roy. Soc. (London)*, **82A**, 147-149 (1909); *Phil. Trans. Roy. Soc.*, **210A**, 199-238 (1910).

<sup>3</sup> Scheel and Heuse, *Ann. Physik*, [4] **37**, 79-95 (1912).

operated, and promise of higher precision. It requires separate determination of the specific heat of the reaction product.

At the suggestion of F. G. Keyes, Dickson<sup>4</sup> made experiments with a continuous-flow calorimeter, studying the heat of neutralization of hydrochloric acid and sodium hydroxide. His result for the approximately 0.05 weight-formal sodium chloride solution produced at 25° was about 2% lower than the corresponding interpolated value of Wörmann,<sup>5</sup> and was too low because of a defect in the calorimeter. With improvements in various details of the apparatus used by him, we have been able to trace the defect, and largely to eliminate it.

The continuous-flow method has been used by F. R. Pratt for heats of dilution.<sup>6</sup> In many details, the apparatus is quite unlike ours, and does not require review here.

### Principle of the Method and General Apparatus

The two liquids which are to react are led down from reservoirs through coils of silver tubes<sup>7</sup> immersed in an upper constant-temperature bath controlled to about 0.1°, then through silver coils immersed in a lower, precision thermostat controlled to about 0.001°, and finally into the mixing calorimeter, which is immersed in the precision thermostat. The mixed liquid passes out of the calorimeter through a narrow tube which permits the mixture to be collected and weighed at suitable time intervals.

In order that equivalent quantities of the two liquids shall mix in a given time, the rates of their flow are adjusted, first with stopcocks and finally with screws which lift or lower the two large bottles used as reservoirs. To preserve equality of flow, each bottle is sealed with a rubber stopper and wax, through which pass both the tube to the calorimeter and also a tube which admits air at a low level. By this "Mariotte bottle" arrangement the hydrostatic head is kept constant during the emptying of the bottles.

One platinum thermometer is immersed in the oil of the precision thermostat and another in the mixed liquid within the vacuum-jacketed space of the calorimeter. The difference in temperature of the two thermometers is a measure of the heating of the mixture by the reaction taking place in the calorimeter, provided that the two liquids have attained the temperature of the thermostat before entering the calorimeter, and that the difference of temperature is corrected for any discrepancy between the two thermometers and for any heat effect due to loss of kinetic energy. From the differences of temperature, measured successively

<sup>4</sup> Dickson, *Thesis* for doctorate, Massachusetts Institute of Technology, June, 1917.

<sup>5</sup> Wörmann, *Ann. Physik*, [4] 18, 775-795 (1905).

<sup>6</sup> Pratt, *J. Franklin Inst.*, 185, 863-895 (1918).

<sup>7</sup> The first pair of silver tubes contained 3 meters each of thin-walled tubing about 2 mm. inside diameter, the second pair contained 2.1 meters each of the same.

at different measured rates of flow, the heat loss can be eliminated, as in the flow method for specific heats. Two rates of flow are mathematically sufficient, but more are observed for precision and also for control of the method and apparatus.

### Calorimeter

The calorimeter is shown in Fig. 1.

The silver tubes are silver-soldered to platinum tubes, which are fused to the glass tubes A of the calorimeter. The two liquids enter the tubes at A, and are squirted from two concentric nozzles at B through an air-space to the bottom of the inverted test-tube C. The mixture travels down the inside wall of the test-tube and up through the narrow space around it to a single nozzle D, whence it emerges to impinge upon a second inverted test-tube E, to travel around the test-tube, then around the platinum thermometer F, finally emerging through the tube G, which connects through a horizontal tube to an upright capillary outlet tube used for controlling in part the rate of flow.

The entire calorimeter, with its metal standard which carries the silver tubes, is immersed in the oil of the precision thermostat to the level shown by the dotted horizontal line in the figure. The reacting liquids are exposed in all directions to the temperature of the thermostat, except in the small area in the vertical direction, which is occupied by the reaction mixture itself flowing upwards. The only doubtful heat loss is that up along the platinum thermometer, and this is located to take advantage of the motion of the mixture. The reacting fluids and the active portion of the thermometer are enclosed in the vacuum jacket J. The jacket walls were not silvered.

The heat loss<sup>8</sup> at the different rates of flow of the present work varied from 6.9 to 2.2% of the heat liberated. From the disposition of the apparatus it is clear, however, that the loss should be regular and capable of calculation, and the straight line graph discussed below gives a test of the reliability of the calculation.

In the construction of the calorimeter, the thin, diaphragm-like portion, I, was introduced to provide elasticity against breakage during the cooling. The vacuum jacket was exhausted, while being baked at about 300°, by a mercury diffusion pump backed by an efficient oil-pump, for about 6 hours. Assuming Newton's law of cooling, the heat loss was found to be about 1 calorie per minute and per degree of temperature difference.

We found, working with a calorimeter almost identical with that used by Dickson, that the theoretical straight line graph discussed below was not realized, after substantial improvements in various

<sup>8</sup> The heat loss was evaluated during the determination of the heat of neutralization.

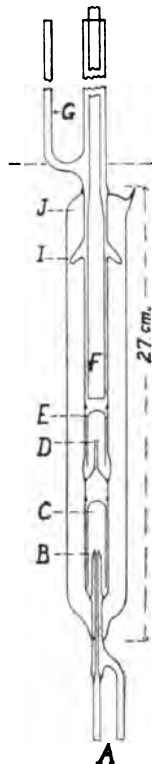


Fig. 1.—Continuous-flow calorimeter.

details of the general apparatus. The maximal temperature difference for a given fixed rate of flow was not reached when the effluent was neutral, but when it was distinctly acid (due to the fact that a small quantity of acid fluid succeeded in escaping the action of the baffles), and the temperature difference varied when the apparatus was not disturbed. When the apparatus was set up so that the flow could be watched by the aid of a sensitive, 2-colored indicator (bromothymol-sulfonephthalein), which was added to the alkali, the difficulties could be traced, the most important defect being that a variable mixture of liquid was delivered to the baffle plates.

The same optical test was applied to the new calorimeter shown in Fig. 1, and only faint and momentary fluctuations of color could be seen in the tube above E, and these only when the rates of flow were very exactly adjusted to neutrality. The fluctuations were limited to small localities in the liquid. When the new calorimeter was tested in a calorimetric experiment the constancy of temperature was much better and the temperature difference was maximal for a neutral effluent.

### Course of the Determinations

The resistance to flow was not the same for the two liquids, owing to unsymmetry in the apparatus, and for each rate of flow, secured by changing the capillary outlet tube, the equality of flow had to be reestablished by adjustment of stopcocks and of the height of the reservoirs. In 5 or 10 minutes, conditions were constant enough to permit the thermometer readings. These were taken every minute alternately for the bath and the mixture for 5 or 10 minutes, and the mean for each thermometer for the period of constancy. Both thermometers showed fluctuations of  $0.001^{\circ}$  and occasionally  $0.002^{\circ}$ , during the period of "constancy."

The time of flow, in minutes per gram of effluent, was determined by collection of the effluent in a tared Erlenmeyer flask during a time of about 5 minutes, measured with a stop watch.

An indirect test was applied to study the efficiency of the silver tubes in bringing to the same temperature the enclosed flowing liquid and the bath.<sup>9</sup> For the main experiment the upper bath was adjusted to equality of the lower bath temperature to about  $0.1^{\circ}$ , by means of a  $0.1^{\circ}$  mercury thermometer checked by the platinum thermometer. In the control experiments it was found that the upper bath could be varied several tenths of a degree without influencing the temperatures of the two platinum thermometers, and when the upper bath temperature was varied enough to change perceptibly the temperature of the reacting mixture, the temperature of the lower bath itself was changed in equal degree.

<sup>9</sup> A similar test was applied by Pratt (Ref. 6), who also placed his (mercury) thermometers in similar positions and referred results to the scale of a single thermometer.

In order to measure the heat produced by friction in the apparatus, pure water was passed through it, at 0.053 and at 0.028 minutes per gram of total effluent, whereupon the two platinum thermometers showed a difference of  $0.039^{\circ}$ . This being greater than the total fall of liquid (about 2 meters) could have produced, the two thermometers were carefully compared by immersion in the same (precision) oil-bath, and it was found that this difference was identical within  $0.001^{\circ}$  with the discrepancy between the thermometers at the temperature of the test. The discrepancy was studied over the range of temperature at which the lower bath was kept during the main experiment, and the correction ( $0.0386^{\circ}$  to  $0.0389^{\circ}$ ) was applied to the thermometer in the bath so that the final results were virtually secured with one thermometer (No. 2).

### Thermometry

The manganin coils of our thermometer bridge were not kept at constant temperature, and the fixed points were not as reproducible as sometimes reported by other workers.<sup>10</sup> Nevertheless, errors in thermometer standardization should have affected our final result by less than 0.1%, since this result is based on temperature differences, and its dependence upon the absolute temperature is relatively small. The ice-points were obtained in the usual way, and also by a technique which showed that the discrepancy between the two thermometers was in no way due to our manipulation. The steam and naphthalene points were obtained in series of measurements which gave best straight lines intersecting the 760 mm. abscissas. The normal boiling point of naphthalene was taken as  $218.04^{\circ}$ . The various constants were, for thermometers No. 1 and 2, respectively:  $R_0$ , 25.3543 and 25.3343;  $R_{100}$ , 35.2305 and 35.2028;  $R_{218}$  46.5210 and 46.4768; fundamental coefficient, 0.00389528 and 0.00389531; and  $\delta$  value, 1.4452 and 1.4755. So far as the final results are concerned, the constants of No. 1 do not matter, because of the mode of referring all temperatures to the scale of No. 2. The  $\delta$  value for No. 2, although the higher of the two, is still rather low, but there is no ground for supposing this to be significant, since a calculation shows that an assumed variation in  $\delta$ , even of 0.05 (or in the form of the correction equation equivalent to such a variation) would affect the temperature differences by about  $0.0001^{\circ}$ , or only 0.01% in the final result.

The thermometers were Leeds and Northrup instruments of the Bureau of Standards pattern.<sup>11</sup> The bridge was a modified Leeds and Northrup calorimetric bridge, in which the contact resistance at the slide wire affected equally the two bridge arms.

<sup>10</sup> Assuming a temperature coefficient for manganin of  $2.10^{-4}$  ohms per ohm and per degree, a difference of  $1^{\circ}$  in the coils affects their resistance so as to show apparent variations in really fixed points of  $0.005^{\circ}$  at  $0^{\circ}$ , and of  $0.009^{\circ}$  at  $218^{\circ}$ .

<sup>11</sup> No. 1 had undergone repairs which may have introduced strains.



It reads directly to 0.00025 ohms, corresponding to about  $0.0025^\circ$ , and the galvanometer sensitivity permits subdivisions to be estimated on the bridge which correspond to  $0.001^\circ$ .

In measuring the temperatures during the flow experiments, the resistance of the coils was always the same, 25.5 ohms, the slide wire being used for the differences between the two thermometers and for the changes of temperature.

### Solutions Used for the Experiments

A good grade of sodium hydroxide purified by alcohol was used. It contained about 0.84 mol-per cent. of sodium carbonate, determined by volumetric titration. In the flow experiments, the end-point was about  $10^{-7}$ , the indicator being bromothymol-sulfonephthalein, so that about 0.42 mol-per cent. of the alkalinity "neutralized" was due to carbonate.

All other titrations were done with weight-burets. The alkali solution was titrated against hydrochloric acid prepared from constant-boiling acid according to Hulett and Bonner,<sup>12</sup> against hydrochloric acid standardized gravimetrically with silver chloride, and against recrystallized potassium hydrogen phthalate. The mean result was that 1 g. of sodium hydroxide solution used for the experiments contained 0.00021111 mols of sodium hydroxide, and neutralized 0.99200 g. of the hydrochloric acid used for the experiments: therefore each gram of sodium chloride solution formed during the neutralization contained 0.00010598 mols of sodium chloride. This figure is the quotient of 0.00021111 divided by  $(1 + 0.992)$ .

The sodium chloride solution formed was thus approximately 0.1 *N*.

TABLE I  
THE EXPERIMENTAL DATA

No.	Time of flow Minutes per gram	Bath temper- ature °C.	Mixture temperature °C.	Difference of temperature °C.	Reciprocal of difference
1	0.0670	32.3296	33.6550	1.3254	0.75449
2	0.0511	32.3105	33.6530	1.3425	0.74488
3	0.0416	32.3277	33.6892	1.3615	0.73448
4	0.0369	32.2934	33.6589	1.3655	0.73233
5	0.0311	32.2899	33.6631	1.3732	0.72823
6	0.0298	32.3075	33.6781	1.3706	0.72961
7	0.0255	32.3085	33.6892	1.3807	0.72427
8	0.0246	32.3085	33.6912	1.3827	0.72322
9	0.0228	32.2915	33.6791	1.3876	0.72067
10	0.0220	32.2975	33.6801	1.3826	0.72327

### Calculation of the Results

The data are presented in Table I. The temperatures are in degrees Centigrade, obtained from the properties of Thermometer No. 2, as stated above.

During the flow experiment, let  $Q$  calories per gram of mixture be generated constantly. If we assume Newton's law of cooling to be exact over the small range of temperatures, each gram of mixture will lose, for every degree of temperature difference,  $qt$  calories, where  $t$  is the time of flow in minutes per gram and  $q$  is the loss of heat from the cooling

<sup>12</sup> Hulett and Bonner, *THIS JOURNAL*, 31, 390-393 (1909).

space (between the mixing tip and the thermometer) per minute and per degree of temperature difference.<sup>13</sup> The temperature difference controlling the loss of heat varies from  $D_0$ , the difference between the temperature immediately developed upon mixing and the temperature of the surrounding bath, to  $D$ , the measured temperature difference at the thermometer, and is then the mean of these values,  $(D_0 + D)/2$ . The heat lost by every gram is therefore  $qt(D_0 + D)/2$ , leaving the quantity,  $Q - qt(D_0 + D)/2$  calories per gram available for raising the temperature; and if it requires  $k$  calories per gram to raise the temperature  $1^\circ$ ,  $k$  being the specific heat of the salt solution, we shall have

$$D = -q/k \cdot t(D_0 + D)/2 + Q/k \quad (1)$$

When  $t$  is zero, the heat loss,  $qt(D_0 + D)/2$ , is also zero, so that the corresponding value of  $D$  is  $D_0$ , the initial temperature difference before any cooling has occurred. Equation 1 can be solved conveniently as follows. The term  $(D_0 + D)/2$  is approximately equal to  $D_0$ , or to  $D$ , leading to the two approximate equations,

$$D = -(D_0 q/k) \cdot t + Q/k \quad (2)$$

$$\text{and } D = -Dt \cdot q/k + Q/k \text{ or } 1/D = -tq/Q + k/Q \quad (3)$$

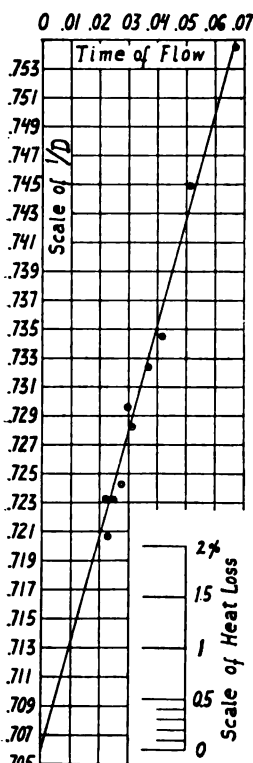
In either case, when  $t = 0$ ,  $D = D_0 = Q/k$ . Either equation can be used to obtain a first approximation. With the present data, Equation 2 gives 1.415 for  $D_0$ , Equation 3 gives 1.417, whereas either of these values, used in Equation 1, leads to an exact value, 1.4160, by the method of least squares. All three equations can be represented by a straight line, by plotting for Equations 1, 2 and 3, respectively, the variables:  $D$ ,  $t(D_0 + D)/2$ ;  $D$ ,  $t$ ; and  $1/D$ ,  $t$ .

Fig. 2 shows how Equation 3 represents the data. The line cuts the axis where  $t = 0$  at  $1/D = 0.706$ , corresponding to  $D_0 = 1.417$ . The data are equally well represented by the other two Equations, 1 and 2. The scale of heat loss in Fig. 2 shows, for a given time of flow, the calculated heat loss as percentage of the total heat liberated. This scale shows also the effect on the final result of uncertainty in the extrapolation to zero time of flow. Thus, let us suppose that the limiting value of  $1/D$  may be 0.709 instead of 0.706. Then the point corresponding to 0.709 on the scale of heat loss is 0.4%, which signifies that the heat of neutralization would be this percentage, 0.4%, lower than the value we actually find.

<sup>13</sup> Our  $t$  is the time for 1 gram to enter the Erlenmeyer weighing flask, and hence the time to leave the mixing tips. Then  $tG$  is the time to fill the cooling space of capacity  $G$  grams, *i. e.*, the time a gram is in the cooling space, on the average. Since the total liquid occupying this space cools  $q$  calories per minute and per degree temperature difference, the corresponding cooling for 1 g. is  $q/G$ , per minute and per degree temperature difference. Therefore  $tG \cdot q/G = qt$ , is the heat lost by the gram, per degree temperature difference.

From Richards and Rowe's<sup>14</sup> figures for the loss of heat capacity on diluting sodium chloride solutions we obtain, by extrapolation,  $k = 0.9913$ . The two end values in their curve for sodium chloride are possibly irregular, according to them; we assumed, however, the curvature necessary to make both end values exact, but the effect upon  $k$  of any error in this assumption is slight, since the molecular heat capacity of our sodium chloride solution is over 9000.

From the exact value, 1.4160, for  $Q/k$ , we find therefore  $Q = 1.4037$



calories per gram mixture. Dividing by the concentration of the solution, 0.00010598 mol. of sodium chloride per gram, we find the heat of neutralization to be 13,245 calories per mol. The method of least squares indicates the "probable error" to be slightly below 0.1% of this value.

The slope of the line in Fig. 2 gives  $q/k = 1.04$ , or  $q = 1.03$ , the probable error being about 2% of this value.

The above result for the heat of neutralization needs to be corrected finally for the presence of carbonate in the hydrate. Through an oversight, the hydrate solution itself was not used for the carbonate determination. The solution was, however, carefully protected from atmospheric carbon dioxide by a tube of soda-lime. From data in Landolt-Börnstein, "Tabellen," 4th edition, it is calculated that the neutralization of  $\text{Na}_2\text{CO}_3$  to the stage of  $\text{NaHCO}_3$  would produce at 18° only 4,600 calories per mol. of hydrochloric acid used, instead of 13,700. The value found above points, therefore, to a still larger value for the heat of neutralization of carbonate-free sodium hydroxide, which is found finally to be 13,280 calories per mol. This value refers to the isothermal heat of neutralization at 32.3°, the mean initial temperature, since the heat capacity of the products was used in the calculation.<sup>15</sup>

Fig. 2.—The reciprocal rise of temperature as a linear function of the time of flow.

<sup>14</sup> Richards and Rowe, *THIS JOURNAL*, 43, 770-796 (1921). We have assumed the specific heat of 0.1 *N* NaCl to be the same at 33° as at 20°. This is equivalent, within about 0.2%, to the assumption that the temperature coefficient of specific heat is the same for the solution as for pure water.

<sup>15</sup> Richards, *ibid.*, 25, 209-214 (1903). We wish to thank Professor Richards for calling our attention to this point.

### Discussion

Since our data give only one point of temperature and concentration, only limited comparison is possible with the data of previous workers. Wörmann<sup>5</sup> determined the heat of neutralization of the 4 combinations between sodium hydroxide, potassium hydroxide, hydrochloric acid, and nitric acid, at 0°, 6°, 18°, and 32°, and his lines are shown in Fig. 3. These are the best straight lines found by him for the mean values at concentrations from 0.25 to 0.1 *N* (normality referring to salt solution formed).

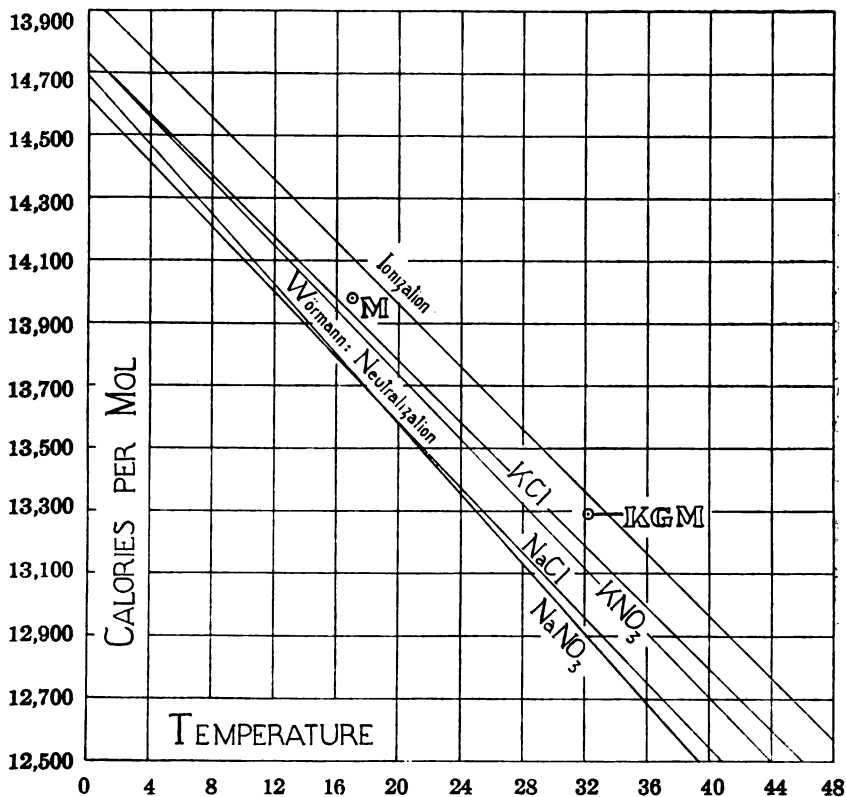


Fig. 3.—Comparison of some heats of neutralization with the heat of ionization calculated by Noyes, Kato and Sosman.

The values for the potassium salts are higher by about 1% than those for sodium. Another line shown in Fig. 3 for comparison is that for the heat of ionization of water, calculated by Noyes, Kato, and Sosman.<sup>16</sup> Our point is shown by the mark KGM. Another point, M, is one obtained by Muller<sup>17</sup> for the heat of neutralization at infinite dilution, obtained

<sup>16</sup> Noyes, Kato and Sosman, *THIS JOURNAL*, 32, 159–178 (1910).

<sup>17</sup> Muller, *Bull. soc. chim.*, [4] 23, 8–13 (1918).

by measuring heats of dilution and of neutralization, this point being the mean for the neutralization of potassium hydroxide with sulfuric acid and with hydrochloric acid.

The agreement of the heat of ionization line with Wörmann's lines has been considered good.<sup>18</sup> Muller's point agrees still better with the ionization line. Our point deviates from it, being smaller, by about 0.5%. The disagreement between our point and Wörmann's line for sodium chloride is, however, outside the accidental errors of both pieces of work, being 2.6%. Differences of concentration cannot explain the discrepancy, as our solution was about 0.1 *N*, and gives a higher heat than his averages over the interval 0.25 to 0.1 *N*, whereas Wörmann found at 0° a higher value for sodium chloride in 0.5 *N* solution than in the more dilute solutions.

We are continuing the work. In the meantime, we wish to point out that Wörmann mentions no correction for carbonate in the alkali solutions, and gives no analysis for carbonate. The presence of about 5.2 mol-per cent. of sodium carbonate in the sodium hydroxide solution would be required to bring the corrected value into agreement with our point and the slope of Richards and Rowe, which is nearly that of the ionization curve. We should hardly expect agreement between the heats of neutralization and of ionization at concentrations where potassium hydroxide is given different values than sodium hydroxide. If, however, a 2.6% correction is justified in the case of sodium hydroxide, a smaller one for potassium hydroxide would suffice to bring the alkalis into better agreement.

### Summary

A continuous-flow calorimeter has been so developed that measurement of the rise of temperature for 10 rates of flow leads to a value of the heat of neutralization, the "probable error" of which is calculated by least squares to be less than 0.1% of the heat itself. Obvious improvements are expected to increase the precision.

For the heat of neutralization resulting in the formation of  $\text{NaCl} \cdot 5.21 \text{H}_2\text{O}$  (about 0.107 *N* sodium chloride) at 32.3°, we find 13,280 calories per mol. Use was made of the specific-heat data of Richards and Rowe, so that the unit is the 18° calorie (equivalent to 4.18 joules).

We should expect our value to be correct within about 0.3%. It is, however, 2.6% higher than the corresponding point on the curve of Wörmann for the same neutralization. This may be due to the absence in his work of a correction for carbonate in the alkali used.

Our point is about 0.5% lower than the corresponding point on the line given by Noyes, Kato and Sosman for the heat of ionization. In our opinion, the 1% difference in the heat, reported by Wörmann, when potassium

hydroxide is substituted for sodium hydroxide in the neutralization, is questionable, because of the lack of a carbonate correction.

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[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF COLUMBIA UNIVERSITY, No. 385]

## THE ABNORMALITY OF STRONG ELECTROLYTES AND THE IONIZATION THEORY OF GHOSH<sup>1</sup>

By JAMES KENDALL

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Many attempts have been made during the past 30 years to account for the failure of the Ostwald dilution law  $\mu_1^2/\mu_\infty \cdot (\mu_\infty - \mu_1) \cdot v = k$  to reproduce the ionization of strong electrolytes. It has been suggested, for example, that the degree of ionization is not correctly represented by the conductivity ratio  $\mu_1/\mu_\infty$ , that the ionization equilibrium is not correctly represented by the equation  $RX \rightleftharpoons R^+ + X^-$ , or that the law of mass action is not applicable to the equilibrium between ions and undissociated molecules. The only alternative theory that has been received with any great degree of favor, however, is one recently developed by Ghosh,<sup>2</sup> which rejects the fundamental assumptions of Arrhenius entirely. It is the purpose of the present article to give a critical analysis of the arguments advanced by Ghosh and others in support of this theory.

**The Postulates of Ghosh.**—The theory, as applied to a uni-univalent salt  $RX$  in solution, is based upon the following postulates: (1) the electrolyte is completely dissociated at all dilutions into oppositely charged radicals  $R^+$  and  $X^-$ ; (2) the arrangement of these charged particles in the solution is analogous to the marshaling of atoms in a simple cubic crystal lattice; (3) the oppositely charged radicals of a salt-molecule  $RX$  form a completely saturated electrical doublet, and the work necessary to separate them is the electrical work done in moving them from their fixed mean distance in the solution to an infinite distance apart; (4) a radical is free to conduct the current only if its kinetic energy is greater than half the work required to separate it from its partner; (5) the distribution of velocities among the particles is according to Maxwell's law.

For salts of other valence types, and for acids and bases, other postulates are made, which will be referred to later. The essential point in the theory of Ghosh is that strong electrolytes are wholly dissociated in solution, partly into *free* and partly into *bound* ions, only the former being capable of conducting the current. The ratio  $\mu_1/\mu_\infty$  consequently ex-

<sup>1</sup> Presented, in part, at the St. Louis meeting of the American Chemical Society, April 14, 1920.

<sup>2</sup> Ghosh, *J. Chem. Soc.*, 113, 449, 627, 707, 790 (1918); 117, 823, 1390 (1920).

presses the *proportion of free ions*, and Ghosh, with the help of the above postulates, derives an equation for the variation of  $\mu$ , with dilution for each type of strong electrolyte which, it is claimed, is in satisfactory agreement with the experimental data. The agreement is, in point of fact, so striking, and so many additional confirmatory points are adduced that Ghosh's conclusion that the validity of the postulates has been thoroughly established is *apparently* perfectly justified. It is true that objections have been raised by Partington<sup>3</sup> and by Chapman and George<sup>4</sup> against certain of Ghosh's assumptions, but the general trend of physical chemists at the present time is obviously towards the acceptance of his theory.<sup>5</sup> Mention may be made, in particular, of articles by Noyes and MacInnes<sup>6</sup> and by Hill.<sup>7</sup> The fact that the main points of Ghosh's theory

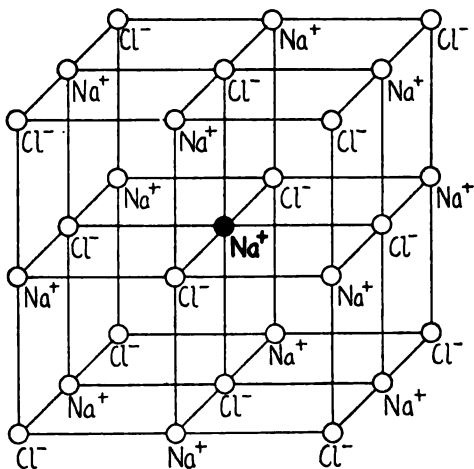


Fig. 1.

are in close harmony with Langmuir's recent work on atomic structure and valence<sup>8</sup> and with the latest results obtained from the examination of salt crystals by X-ray analysis<sup>9</sup> has undoubtedly predisposed many investigators in its favor.

If it could be shown, however, that the postulates of Ghosh are inconsistent with one another, that they are at variance with carefully established experimental data, that the equations which Ghosh employs do not follow from his postulates, or

that the agreement between these equations and the results of experiment is fictitious, then the theory in its present form would of necessity become unacceptable. In the following pages it will be shown that the theory is indeed vulnerable at all of the above points, and that many of Ghosh's conclusions must in consequence be modified or rejected.

<sup>3</sup> Partington, *Trans. Faraday Soc.*, **15**, 111 (1919).

<sup>4</sup> Chapman and George, *Phil. Mag.*, [VI] **41**, 799 (1921).

<sup>5</sup> For example, at a recent symposium on the present position of the ionization theory [*Trans. Faraday Soc.*, **15**, 1-178 (1919)], the opinion was expressed by Sand (p. 171), "it seemed not improbable that Ghosh's theory would rank as the most important advance in the theory of electrolytic conduction since the enunciation of the Ostwald-Planck dilution law." See also Walker, "Introduction to Physical Chemistry," Macmillan and Co., 1919, p. 286.

<sup>6</sup> Noyes and MacInnes, *THIS JOURNAL*, **42**, 239 (1920).

<sup>7</sup> Hill, *ibid.*, **43**, 254 (1921).

<sup>8</sup> Langmuir, *J. Ind. Eng. Chem.*, **12**, 386 (1920); *THIS JOURNAL*, **42**, 274 (1920).

<sup>9</sup> "Ann. Reports Chem. Soc.," **16**; 209 (1919); **17**, 2 (1920).

**Inconsistency of the Postulates.**—The second and the third postulates of Ghosh are absolutely incompatible. If the marshaling of the oppositely-charged particles of a salt such as sodium chloride in solution is analogous to the arrangement of the atoms in the crystalline structure (see Fig. 1), then no positively charged particle  $\text{Na}^+$  is specifically attached to any particular negatively charged particle  $\text{Cl}^-$  to give a salt-molecule  $\text{NaCl}$  or to form a completely saturated electrical doublet. Any atom will be kept in a definite mean position in the cubic lattice by the electrical forces exerted between it and all of the surrounding atoms, and cannot form a neutral doublet with any one of the 6 oppositely charged atoms in immediate proximity to it without destroying the whole basis of the crystal structure.

Ghosh's calculation of the electrical work required to separate "the component ions of a salt-molecule," where  $E$  is the charge on each ion,  $D$  the dielectric constant of water, and  $r$  the distance between oppositely charged ions, leads therefore to an entirely incorrect result.

**Calculation of the Electrical Work Necessary to Separate the Component Ions of a Gram-molecule.**—The true value of  $A$ , the electrical work necessary to disperse to infinite dilution the component radicals of a gram-molecule of dissolved salt, if arranged according to the cubic space lattice, may be obtained as follows.

Consider one particular atom, such as the central  $\text{Na}^+$  in Fig. 1, and sum up the work necessary to disperse the atoms immediately surrounding it, taking into account only the force exerted between each atom and the central  $\text{Na}^+$ . There are, first of all, 6  $\text{Cl}^-$  particles at a distance  $r$ . The work to separate these to an infinite distance is  $6 \frac{E^2}{Dr}$ . The cubes shown in the diagram also contain, however, 12  $\text{Na}^+$  particles at a distance  $\sqrt{2} r$ , and 8  $\text{Cl}^-$  particles at a distance  $\sqrt{3} r$ . The total work required to disperse the particles forming these cubes is therefore

$$\frac{E^2}{Dr} \cdot \left( 6 - \frac{12}{\sqrt{2}} + \frac{8}{\sqrt{3}} \right) = 2.134 \frac{E^2}{Dr}.$$

The particles in more remote cubes must next be considered. If we pack one more layer of cubes all around those represented in the diagram, and sum up the work necessary to disperse each particle, as before, we obtain for this second layer of particles

$$\frac{E^2}{Dr} \cdot \left( -\frac{6}{2} + \frac{24}{\sqrt{5}} - \frac{24}{\sqrt{6}} - \frac{12}{\sqrt{8}} + \frac{24}{\sqrt{9}} - \frac{8}{\sqrt{12}} \right) = -0.617 \frac{E^2}{Dr}.$$

Continuing out into space, we obtain for the next four layers the values  $+0.398 \frac{E^2}{Dr}$ ,  $-0.295 \frac{E^2}{Dr}$ ,  $+0.234 \frac{E^2}{Dr}$  and  $-0.192 \frac{E^2}{Dr}$  respectively.

The work for successive layers is therefore opposite in sign and steadily diminishing in magnitude. The rate of diminution, after the second layer,



is very nearly expressed by the simple relation (layer work)  $\times$  (layer number) = constant.

We are therefore able to evaluate the work necessary to separate one particular particle from all surrounding particles; it is the limit of the convergent series

$$\frac{E^2}{Dr} \cdot (2.134 - 0.617 + 0.398 - 0.295 + 0.234 - 0.192 + \dots) = 1.75 \frac{E^2}{Dr}.$$

Now, in one gram-molecule of dissolved salt there are  $2N$  particles,  $N$  being Avogadro's number. The total electrical work  $A$  necessary to disperse these will be  $A = 1.75 NE^2/Dr$ . (The factor 2 falls out of this equation, since in summing up the *total work* the force necessary to separate any 2 particles is considered twice, once for the first and once for the second particle.)

The value here obtained is significantly different from that derived by Ghosh,  $NE^2/Dr$ . Consequently all of the equations employed by Ghosh, which utilize the relation  $A = NE^2/Dr$ , stand in need of correction.

**The Distribution of Velocities.**—Ghosh has calculated that the number of free ions in a gram-molecule of dissolved salt is given by the expression  $2N \cdot e^{-\frac{A}{2RT}}$ . It has been shown by Chapman and George<sup>4</sup> that this calculation is erroneous. Maxwell's law for the distribution of velocities leads to an entirely different and much more complicated expression for the number of particles which possess a kinetic energy in excess of the critical value.<sup>10</sup> All of the equations employed by Ghosh which utilize the above expression for the number of free ions stand also, therefore, in need of correction.

**The Variation in the Proportion of Free Ions with Dilution.**—The equation which Ghosh finally derives from his five postulates is

$$\frac{N \cdot E^2 \cdot \sqrt[3]{2N}}{D \cdot \sqrt[3]{v}} = 2RT \ln \frac{1}{\alpha}$$

where  $\alpha$  is the proportion of free ions at dilution  $v$ . For aqueous solutions at  $18^\circ$ , this reduces to

$$\log \alpha = -0.1616/\sqrt[3]{v}.$$

Since  $\alpha = \mu_s/\mu_\infty$  (or, more accurately,  $\mu_s\eta_s/\mu_\infty\eta_\infty$ , where  $\eta_s$  and  $\eta_\infty$  are the viscosities of the solution and the solvent respectively), the validity of this relationship can be directly tested against the experimental data.

Two separate points are here involved. In the first place, *all electrolytes of the same type should give identical values for  $\mu_s/\mu_\infty$  at any given dilution.* In the second place, *the variation of  $\mu_s/\mu_\infty$  with dilution should be as represented by the above equation.*

<sup>10</sup> See Jeans, "The Dynamical Theory of Gases," Cambridge Univ. Press, 1916, pp. 34-5.

**Are All Electrolytes of the Same Type Equally Ionized?**—This point has been called in question by Partington,<sup>8</sup> who presents extensive data to show that considerable divergences exist in the experimental values of  $\mu_v/\mu_\infty$  for different electrolytes. In reply, Ghosh<sup>11</sup> objects to the values of  $\mu_\infty$  employed by Partington, and deduces alternative values for the alkali chlorides which make  $\mu_v$  throughout the range  $v = 10$  to  $v = 5000$  practically identical in all cases.

It is impossible to settle this dispute satisfactorily at the present time, since the value for  $\mu_\infty$  derived for any electrolyte depends upon the form of the equation used to extrapolate the experimental data to infinite dilution, and the choice of any particular equation largely predetermines the issue. It is true that many chemists<sup>12</sup> have preceded Ghosh in postulating identical ionization values for restricted series of salts of similar character at high dilutions, and that the deviations which become evident at higher concentrations may quite plausibly be ascribed to specific effects, such as changes in ionic mobilities. At concentrations approaching normal, indeed, the diameter of the ions becomes appreciable with respect to the distance between them, and salts which furnish ions of large diameter might be expected to give significant and specific variations from the simple equations of Ghosh. All this being granted, the position of advantage in the  $\mu_\infty$  controversy still appears to lie with Partington. The values for  $\mu_\infty$  employed by Partington are all taken *directly* from Kohlrausch, as extrapolated by him from his own data. The values employed by Ghosh *assume* that the careful conductivity measurements of Kohlrausch and his co-workers at high dilutions are in error to the extent of 1–2%, and it is extremely unlikely that this assumption is justified.<sup>13</sup>

In the case of potassium chloride, indeed, we have positive evidence in favor of Partington. The value of  $\mu_\infty$  which Kohlrausch obtains for this salt is 129.90. The value deduced by Ghosh is 132.2. The recent determinations of Washburn and Weiland,<sup>14</sup> carried out to a remarkable degree of precision at exceedingly high dilutions, lead to the value 129.64.

**Is the Variation of Ionization with Dilution Represented by the Equation of Ghosh?**—The experimental data for potassium chloride are shown in Table I, p. 722. From  $v = 10$  to  $v = 500$  the equivalent conductivities of Kohlrausch and Maltby<sup>15</sup> have been taken, the usual viscosity corrections being applied. From  $v = 1000$  to  $v = 10000$  the

<sup>11</sup> Ghosh, *Trans. Faraday Soc.*, **15**, 154 (1919).

<sup>12</sup> For example, Noyes and Falk, *THIS JOURNAL*, **34**, 475 (1912). Lewis, *ibid.*, **34**, 1643 (1912). Washburn, *ibid.*, **40**, 151 (1918).

<sup>13</sup> See Kendall, *ibid.*, **39**, 19 (1917).

<sup>14</sup> Washburn and Weiland, *ibid.*, **40**, 131 (1918).

<sup>15</sup> Landolt-Börnstein, "Tabellen," 1912, p. 1102.

results are those of Washburn and Weiland.<sup>16</sup> The end-value of the latter investigators has been used throughout.

The values for  $\alpha$  derived from Ghosh's equation are given in the third column. The last columns headed " $\alpha$  (Corrected)" show respectively: (I) the values for  $\alpha$  obtained when the expression  $A = 1.75 NE^2/D\tau$  is substituted for that employed by Ghosh, (II) the values for  $\alpha$  obtained when the Chapman and George correction is made, (III) the effect of both of the above corrections.

TABLE I  
Proportion of Free Ions  
Potassium chloride in water at 18°

$v$	$\alpha$ (Expt.)	$\alpha$ (Ghosh)	$\alpha$ (Corrected)		
			I	II	III
10	0.8625	0.8410	0.7393	0.9511	0.8950
50	0.9245	0.9041	0.8380	0.9775	0.9494
100	0.9440	0.9230	0.8691	0.9838	0.9638
500	0.9741	0.9542	0.9213	0.9926	0.9834
1000	0.9816	0.9634	0.9370	0.9946	0.9883
5000	0.9926	0.9784	0.9626	0.9972	0.9945
10000	0.9953	0.9829	0.9702	0.9980	0.9959

It will be seen that the equation used by Ghosh gives values somewhat lower than the experimental throughout the whole dilution range. The application of the first correction leads to much lower values. The second correction, on the other hand, gives results considerably higher than the experimental. The two corrections together largely cancel each other's effect, and a series of values is obtained only slightly higher than the experimental. The differences at the higher concentrations, however, are far beyond the limits of experimental error.

It does not follow, of course, from the above table that Ghosh's theory is fundamentally invalid. Further modification of the postulates might very conceivably suffice to bring the calculated and experimental values into satisfactory agreement. At this point we may profitably note, with respect to the fifth postulate, that Maxwell's law for the distribution of velocities is derived on the assumption that the particles are not electrically charged and are perfectly free to move in space. Its extension to positively and negatively charged particles, the mean disposition of which conforms to a definite space-lattice, certainly requires justification.

Whether Ghosh's second postulate—that the arrangement of the oppositely-charged radicals of a salt in solution is according to a definite space-lattice—is itself acceptable, is a point we shall return to later. In the sections immediately succeeding, the concordance claimed by Ghosh to exist between the equations resulting from his theory and the observations of previous workers will be examined. In order to make the criticisms on the various topics discussed quite independent of those which

<sup>16</sup> Ref. 14, p. 146.

have preceded, Ghosh's original equations are used throughout. So many different points are involved that the treatment of each is necessarily brief and, for space considerations, the argument is confined almost entirely to uni-univalent electrolytes.

**The Variation of Equivalent Conductivity with Dilution.**—To avoid the difficulty introduced by the uncertainty in  $\mu_{\infty}$ , Ghosh prefers to test the validity of his equation for uni-univalent electrolytes in aqueous solution at 18°,

$$\log \alpha = -0.1616/\sqrt[3]{v}$$

by throwing it into the form

$$\log \mu_v - \log \mu_{100} = 0.1616 \left( \frac{1}{\sqrt[3]{100}} - \frac{1}{\sqrt[3]{v}} \right).$$

The value of  $\mu_v$  for the dilution  $v = 100$  is thus made the basis of calculation for  $\mu_v$  at other dilutions, and incidentally is also used to evaluate  $\mu_{\infty}$ .

Equations of a similar nature are derived by Ghosh for salts of two other valence types, barium chloride and magnesium sulfate, under the assumption that the space-lattice arrangement of the charged particles in solution corresponds in each case to the crystal structure. All three equations are tested<sup>17</sup> against the experimental data of Kohlrausch, and the agreement between the observed and calculated values of  $\mu_v$  for dilutions from  $v = 10$  to  $v = 5000$  is characterized as "remarkably good," "rarely greater than 1 per cent."

Is this agreement really remarkable? Let us take the first salt listed, potassium chloride. According to the figures given,  $\mu_v$  varies throughout the whole concentration range by 17.1 units only, from 112.0 at  $v = 10$  to 129.1 at  $v = 5000$ . If now we assume, as Ghosh does, that the calculated and observed values of  $\mu_v$  are *identical* at a point in the middle of this narrow range, *i. e.*, 122.5 at  $v = 100$ , the concordance of calculated and observed values becomes more a matter of necessity than of merit. When  $\mu_v$  varies from  $\mu_{100}$  at the utmost by only 10%, as is the case with all of the uni-univalent electrolytes tested by Ghosh, then a divergence of 1 unit, which is frequent in the table, is equivalent to an error of 1 in 10. The fundamental validity of the equation can scarcely be confirmed by evidence of this character; all that has been demonstrated is that it reproduces the observed results fairly well over a restricted range, and other interpolation equations<sup>18</sup> are known which possess equal, if not superior, accuracy over the same interval.

If we could prove satisfactory agreement over a more extended range, the above criticism would naturally no longer hold. At concentrations above  $v = 10$ , however,  $\mu_v$  loses much of its theoretical significance, in

<sup>17</sup> Ghosh, *J. Chem. Soc.*, 113, 455-6 (1918).

<sup>18</sup> See Washburn, *Ref. 12*, p. 122.

consequence of the increasing magnitude of the arbitrary corrections necessary for viscosity and ionic mobility changes. At concentrations below  $v = 5000$ , on the other hand, few determinations of sufficient precision are available. It is highly significant that the equation cannot be extended, in the case of potassium chloride, to give agreement with the very accurate determinations of Washburn and Weiland<sup>14</sup> between  $v = 1000$  and  $v = 100,000$ . The calculated values deviate more and more from the observed as the dilution is increased, the final  $\mu_{\infty}$  values differing by as much as 2%, far beyond the limits of experimental error.

In the majority of cases, indeed, the actual agreement between calculated and observed values for  $\mu_v$  between  $v = 10$  and  $v = 5000$  is by no means so striking as indicated by Ghosh in his three tables. Comparison of these tables with the original data of Kohlrausch and his co-workers<sup>19</sup> discloses the fact that *in no fewer than 39 out of 75 instances the value for  $\mu_v$  (obs.) presented by Ghosh differs from that recorded by Kohlrausch.* The difference frequently exceeds a whole unit. The remarkable agreement claimed by Ghosh is therefore largely fictitious.

**The Temperature-coefficient of the Ratio  $\mu_v/\mu_{\infty}$ .**—The next point considered by Ghosh<sup>20</sup> is the variation in the ratio  $\mu_v/\mu_{\infty}$  with temperature, due to the variation in the dielectric constant of water. The experimental data for potassium chloride at 18° and 100° are utilized to show that the observed diminution of  $\mu_v/\mu_{\infty}$  at a fixed dilution with increase of temperature corresponds with the variation calculated from the Ghosh equation. For the dielectric constant of water at 100°, the value 52.6 is employed. The data for  $\mu_v/\mu_{\infty}$  at two dilutions,  $v = 12.5$  and  $v = 100$ , at 18° and 100° are tabulated, and it is noted once more that the "coincidence" between the calculated and observed values is "remarkable."

It is unfortunate for the theory of Ghosh, therefore, that all of the calculated values in this table are wrong. At 18° the errors of calculation are relatively small; for  $v = 12.5$  Ghosh's equation gives  $\mu_v/\mu_{\infty} = 0.852$  (instead of 0.854), while for  $v = 100$  it gives 0.923 (instead of 0.930). At 100°, however, the equation utilized by Ghosh for the variation of the dielectric constant of water with temperature<sup>21</sup> really leads to the value 58.4, not to 52.6. The *true* calculated values for  $\mu_v/\mu_{\infty}$  at 100° according to the equation of Ghosh are, at  $v = 12.5$ , 0.841 (instead of 0.826) and, at  $v = 100$ , 0.917 (instead of 0.909).

In addition to this, the experimental figures for the ionization of potassium chloride at 18° are not accurately transcribed, the value given

<sup>19</sup> Kohlrausch, "Gesammelte Abhandlungen," Barth, Leipzig, 1911, vol. 2; Landolt-Börnstein, "Tabellen," 1912.

<sup>20</sup> Ref. 17, p. 457.

<sup>21</sup> Ref. 15, p. 1213.

by Noyes and Coolidge<sup>22</sup> at  $v = 12.5$  being 0.873 (instead of 0.870) and, at  $v = 100$ , 0.942 (instead of 0.940).

These corrections, it will be noted, vitiate entirely the claim made by Ghosh that the diminution of the ratio  $\mu_v/\mu_\infty$  with increase in temperature has been quantitatively explained.

**The Electrical Conductivity of Non-aqueous Solutions.**—The whole of Ghosh's second paper<sup>23</sup> is devoted to this topic; 28 tables of data are presented, and it is again concluded that the validity of the equations is "completely confirmed." The experimental results employed are mainly from the work of Carrara<sup>24</sup> and of Walden.<sup>25</sup> In order to obtain satisfactory agreement between calculated and observed values for Walden's "normal electrolyte" tetra-ethyl-ammonium iodide, however, Ghosh finds it necessary to assume that this salt, in most non-aqueous solvents, first *polymerizes* and then *dissociates not as a binary but as a ternary electrolyte*, giving the ions  $2\text{NEt}_4^+$  and  $\text{I}_3^-$ . The same assumption is made for sodium and potassium iodides in acetonitrile and in pyridine, respectively, while for ammonium iodide in acetone an additional postulate is involved, namely that the  $\text{NH}_4^+$  ions are displaced diagonally towards the  $\text{I}_3^-$  ions in the space lattice.

These assumptions have been attacked by Partington<sup>26</sup> as purely arbitrary, and there is no question that Ghosh chooses his polymerizing solvents in a most peculiar manner. Thus tetra-ethyl-ammonium iodide is regarded as a binary electrolyte in acetaldehyde and acetone, liquids with dielectric constants of approximately 20, while in formamide, a solvent closely resembling water, with a dielectric constant of 84, the same salt is treated as a ternary electrolyte.

Obviously, if variants of the normal space lattice are admissible, it will always be possible to select one which will lead to an equation reproducing the observed values for  $\mu_v$  for any particular solution within the limits of experimental error, especially when the error limits are relatively large, the range of dilutions is small, the variation in  $\mu_v$  throughout this range is small, and the equation is thrown into a form which makes  $\mu_v$  (calc.) and  $\mu_v$  (obs.) identical in the middle of the range. What positive evidence, then, does Ghosh adduce in support of his new assumptions to rescue them from the suspicion of being merely arbitrary?

The statement that iodine tends to form univalent complex ions such as  $\text{I}_3^-$  and  $\text{I}_5^-$  has no bearing at all upon the ability of iodine ion to unite

<sup>22</sup> Noyes and Coolidge, *Carnegie Inst. Pub.*, 63, 53 (1907). The reference given by Ghosh [*Z. physik. Chem.*, 46, 323 (1903)] does not contain any of the experimental values which he employs.

<sup>23</sup> Ref. 17, p. 627.

<sup>24</sup> Carrara, *Gazz. chim. ital.*, [i] 26, 119 (1896).

<sup>25</sup> Walden, *Z. physik. Chem.*, 54, 129 (1906).

<sup>26</sup> Ref. 2, p. 113.

with itself to form a divalent ion  $I_2^{=}$ . Furthermore, as we shall see later, Ghosh's equation for uni-univalent electrolytes in solvents of low dielectric constant fails just as inevitably with other salts as it does with iodides. It is true, as Ghosh remarks, that the consensus of opinion among electrochemists is generally in favor of complex molecules in non-aqueous solutions. This opinion, however, is based on the fact that freezing-point depressions and boiling-point elevations obtained for salts in solvents of low dielectric constant are abnormally small,<sup>27</sup> and it has been clearly established in recent articles by Hildebrand<sup>28</sup> that such abnormalities must be ascribed, in general, to differences in the internal pressures of the components of the solution, *not* to association of the solute. The only other argument advanced by Ghosh in proof of the abnormality of tetra-ethyl-ammonium iodide in certain solvents is that "the exact coincidences between the observed and calculated values leave no room for doubt as to the mode of dissociation." This argument loses weight when it is found, once more, on examination of the original tables, that *in as many as 31 instances in this article Ghosh's values for  $\mu$ , (obs.) do not agree with the actual experimental data.*

**The Molecular Number  $i$  and the Clausius Theorem.**—In his third article,<sup>29</sup> Ghosh combines his equation:  $A = 2RT \ln 1/\alpha$  with the Clausius theorem:<sup>30</sup>  $PV = \frac{2}{3}$  kinetic energy  $- \frac{1}{3}$  virial and derives, for a uni-univalent salt in aqueous solution, the following expression for the molecular number  $i$

$$i = 2 \left( 1 - \frac{1}{3} \ln \frac{1}{\alpha} \right).$$

He then purports to show that this expression gives better agreement with the experimental values for  $i$ , as obtained from freezing-point depression measurements for binary electrolytes, than does the Arrhenius equation  $i = 1 + \alpha$ . Similarly successful comparisons having been made for typical ternary salts, Ghosh concludes that the validity of his fundamental equations has now been completely demonstrated; "in fact, a complete theory of dilute salt solutions has been propounded."

In point of fact, however, Ghosh never tests the Arrhenius equation connecting experimental conductivity ratios with experimental freezing-point depression abnormalities at all. To evaluate  $i$  at various dilutions he substitutes, in both of the above equations, not the *experimental* value for  $\alpha$ ,  $\mu_s/\mu_\infty$ , but the *theoretical* value for  $\alpha$  calculated from his own equation.

<sup>27</sup> See Turner, "Molecular Association," Longmans, Green and Co., 1915, pp. 46-8.

<sup>28</sup> Hildebrand, *THIS JOURNAL*, 38, 1452 (1916); 42, 2180 (1920).

<sup>29</sup> Ref. 17, p. 707.

<sup>30</sup> Compare Milner, *Phil. Mag.*, [vi] 23, 551 (1912); 25, 747 (1913).

$$\frac{N.E^2.\sqrt[3]{2N}}{D.\sqrt[3]{v}} = 2 RT \ln \frac{1}{\alpha}$$

All that Ghosh really shows, therefore, is that this equation gives values for  $\alpha$  which vary with dilution in such a manner that the expression  $2\left(1 - \frac{1}{3} \ln \frac{1}{\alpha}\right)$  reproduces the freezing-point depression values for  $i$  more closely than does the expression  $1 + \alpha$ . The values obtained from this latter expression, however, are far from being identical with those derived from the experimental conductivity data for uni-univalent salts,<sup>31</sup> as may be seen from the following table. The calculated values for the expression  $2\left(1 - \frac{1}{3} \ln \frac{1}{\alpha}\right)$  and the experimental freezing-point depression values<sup>32</sup> for  $i$  are also here included.

TABLE II  
MOLECULAR NUMBER  $i$  FOR SALTS OF TYPE RX

$v$	2	5	10	20	50	100
$i = 1 + \alpha$ (calc. from Ghosh equation).	1.748	1.808	1.844	1.875	1.906	1.924
$i = 1 + \alpha$ (expt. from conductivity)....	1.771	1.821	1.855	1.885	1.918	1.938
$i = 2\left(1 - \frac{1}{3} \ln \frac{1}{\alpha}\right)$ .....	1.806	1.859	1.887	1.910	1.934	1.947
$i$ (expt. from freezing-point depression) .	1.804	1.837	1.865	1.887	1.925	1.937

From this table it is evident that the Arrhenius equation:  $i = 1 + \alpha$ , where  $\alpha = \mu_0/\mu_\infty$  (expt.), gives better agreement with the freezing-point depression data than does the Ghosh-Clausius equation, except at the highest concentration  $v = 2$ . The deviations at the higher concentrations, indeed, are only such as might be expected from the fact that van't Hoff's law  $\pi V = RT$  cannot be valid for strong electrolytes.<sup>33</sup> As the dilution is increased, the superiority of the Arrhenius expression becomes manifest. This superiority is indisputably confirmed on examination of the later and more accurate freezing-point depression data of Adams<sup>34</sup> and of Hall and Harkins.<sup>35</sup>

**The Ionization of Strong Acids.**—Aqueous solutions of strong acids like hydrochloric acid and of strong bases like potassium hydroxide give much higher values for  $\mu_0/\mu_\infty$  than do uni-univalent salts at equivalent dilutions, and do not exhibit even approximate agreement with the equation of Ghosh. In his fourth paper,<sup>36</sup> Ghosh attempts to account for

<sup>31</sup> Noyes and Falk, Ref. 12, p. 476.

<sup>32</sup> Noyes and Falk, THIS JOURNAL, 32, 1027 (1910).

<sup>33</sup> See Washburn, *ibid.*, 32, 485 (1910); and, more particularly, Bates, *ibid.*, 37, 1421 (1915).

<sup>34</sup> Adams, *ibid.*, 37, 495 (1915).

<sup>35</sup> Hall and Harkins, *ibid.*, 38, 2658 (1916).

<sup>36</sup> Ref. 17, p. 790.



this by postulating that the ratio  $\mu_h/\mu_\infty$  is not, for acids and bases dissolved in water, the true expression for the proportion of free ions, since the water molecules also take an active part in the transmission of the current. It is assumed that a hydrogen ion or an hydroxyl ion, striking against a molecule of water, may cause the latter to undergo dissociation into  $H^+$  and  $OH^-$ , and that one of these unites with the original ion to regenerate a molecule of water while the other shoots off as a charged particle. If this process of dissociation and recombination is instantaneous, the electric charge is thus carried instantaneously through a distance proportional to the diameter of the water molecule, and the apparently abnormal mobilities of the hydrogen and hydroxyl ions in aqueous solution are explained.

This is an old suggestion of Arrhenius.<sup>37</sup> It introduces several points of difficulty. Why should the impacts of other ions on these dissociable water molecules be entirely innocuous? Why should the mobilities of other ions approach those of  $H^+$  and  $OH^-$  at high temperatures, as has been shown by Noyes and his co-workers?<sup>38</sup> One would rather expect the opposite, since water molecules should be more readily dissociable as the temperature is raised, and the impacts between them and  $H^+$  and  $OH^-$  ions are certainly more violent. How can the fact that the ratio  $\mu_h/\mu_\infty$  for hydrochloric acid at high temperatures is *less* than that of potassium chloride at an equivalent dilution<sup>39</sup> be explained? Finally, since it is admitted<sup>40</sup> that the constituent radicals of the water molecule are oppositely charged, why should these radicals also not attempt to take up a space-lattice arrangement and contribute towards the production of free ions in all aqueous solutions?

The last of these points—the rôle of the solvent in ionization—will be taken up in the concluding sections. Let us assume, for the present, that Ghosh's new postulate is valid, and examine the consequences.

First of all, assuming that the true value of  $\alpha$  for strong acids like hydrochloric acid at any given dilution is the same as that of uni-univalent salts, Ghosh develops an equation by which the real mobility  $U_{H^+}$  of the hydrogen ion and the conductivity  $C_1$  due to the water may be evaluated from conductivity data. For acids,  $U_{H^+} = 152$  and  $C_1 = 198.5$  at  $25^\circ$ ; for bases,  $U_{OH^-} = 109$  and  $C_1 = 66$ . Tables are given to show that the calculated variation of  $\mu_h$  with dilution for strong acids and bases, when these values are substituted in Ghosh's equation, is always in agreement with the experimental data within 0.5%. Unfortunately the experimental values for  $\mu_h$ , in any single case, vary only from 3 to 6% throughout

<sup>37</sup> Arrhenius, "Theories of Solutions," Yale University Press, 1912, p. 139.

<sup>38</sup> Noyes, *et al.*, *Carnegie Inst. Pub.*, 63, 336 (1907).

<sup>39</sup> Ref. 38, p. 339.

<sup>40</sup> Ghosh, Ref. 11, p. 159.

the range of dilutions examined, so that the test is not very stringent. More definite support for the validity of his contention that the true value for  $\alpha$  is the same for strong acids and bases as for salts is sought by Ghosh<sup>40</sup> from the work of Ellis<sup>41</sup> on activity-coefficients by the electromotive-force method. Reference to a table recently published by Noyes and MacInnes<sup>42</sup> will show, however, that the most accurate data in this important field, *including the results of Ellis*, indicate conclusively that the activity-coefficients for hydrochloric acid, potassium hydroxide and potassium chloride diverge considerably, and are in no single case in agreement with the calculated values of Ghosh.

**The Ionization of Weak Acids.**—Still more convincing evidence against Ghosh's theory is obtained from the results of its application to typical weak electrolytes like acetic acid. These are assumed to give both undissociated molecules and ions in solution, their ionization equilibria being expressed by the equation:  $(\alpha x)^2/(1-x) \cdot v = k$ , where  $x$  is the fraction dissociated and  $\alpha$  the proportion of free ions in this fraction. For any ionic concentration  $x/v$ ,  $\alpha$  can be calculated, and is so very nearly equal to 1 at all dilutions (according to Ghosh) that the above equation becomes identical with Ostwald's dilution law for very weak acids.

The *actual data for acetic acid* at 25° are presented in Table III below. The first column shows the dilution and the second the observed conductivity.<sup>43</sup> In the third and fourth columns  $x$  and  $\alpha$ , as calculated from the equations of Ghosh, are shown. The fifth column gives the dissociation constant derived from these values, the last column the dissociation constant obtained on the basis of the original Arrhenius theory.

TABLE III  
ACETIC ACID, 25°

$v$	$\mu_v$	$x$	$\alpha$	100 $k$ (Ghosh)	100 $k$ (Arrhenius)
13.57	6.086	0.01585	0.9613	0.001740	0.001845
27.14	8.591	0.02234	0.9655	0.001754	0.001851
54.28	12.09	0.03138	0.9693	0.001759	0.001849
108.56	16.98	0.04399	0.9727	0.001765	0.001849
217.1	23.81	0.06160	0.9757	0.001773	0.001851
434.2	33.22	0.08584	0.9784	0.001777	0.001849
868.4	46.13	0.1191	0.9809	0.001783	0.001850
1737.0	63.60	0.1640	0.9831	0.001790	0.001854

Evidently  $\alpha$  diverges appreciably from unity throughout the whole range, although at the last dilution given the ionic concentration is less than 0.0001 *N*. In consequence of this variation in  $\alpha$  with dilution, the theory of Ghosh involves a steady increase in the ionization constant, as illustrated by the figures in the fifth column. The exact applicability

<sup>41</sup> Ellis, *THIS JOURNAL*, 38, 759 (1916).

<sup>42</sup> Ref. 6, p. 243.

<sup>43</sup> Kendall, *J. Chem. Soc.*, 101, 1283 (1912).

of the Ostwald dilution law to weak acids like acetic acid and weak bases like ammonia must therefore be devoid of all theoretical basis, and the constant values for  $k$  obtained for so many weak electrolytes by so many different observers (as, for example, in the last column of the preceding table) are presumably entirely fortuitous! A more cogent argument *against* the validity of Ghosh's assumptions can scarcely be conceived.

**The Ionization of Transition Acids.**—Ghosh claims, however, to have demonstrated the applicability of his formula also to "the entire range of transition electrolytes." The equation developed for determining  $x$  for solutions of such electrolytes<sup>44</sup> is, it may be noted, erroneous, since it involves the use of the relationship  $\alpha = 1 - K.(x/v)^{1/2}$ , which is derived<sup>45</sup> under the condition that  $\mu_0$  is only slightly less than  $\mu_\infty$ .

It has been shown by the present author<sup>46</sup> that the dissociation constants for transition acids decrease towards a limiting value  $k_\infty$  as the dilution is increased. The variation in  $\alpha$ , calculated according to the Ghosh theory, is (as in the case of acetic acid above) in the opposite direction. The application of the Ghosh equation  $(\alpha x)^2/(1-x) \cdot v = k$  to transition electrolytes consequently gives, owing to the counterbalancing of these two factors, a fairly satisfactory value for  $k$  throughout a limited dilution range. Nevertheless, if the examination is extended to high dilutions, where  $k$  (Arrhenius) is practically constant while  $\alpha$  is still increasing, the inconstancy of  $k$  (Ghosh) becomes obvious. The stronger the acid, the more rapidly do the values for the latter expression increase. The first stages of this inevitable increase are quite evident in all of the four tables for transition acids presented by Ghosh, although in each case the data for the highest dilutions, where the variations in  $k$  become much more pronounced, are prudently omitted.

**The Electrical Conductivity of Pure Salts in the Solid and Fused States.**—Most of Ghosh's fifth paper<sup>47</sup> is occupied with the derivation of equations for the variation of the specific conductivity of a solid salt with temperature, and the presentation of experimental data in support of these equations. At first sight, the concordance of the observed figures with those calculated from Ghosh's final equation<sup>48</sup>

$$\frac{W_0(T_2 - T_1)}{2R} \left( \frac{1}{T_1 T_2} + \frac{1}{T_\infty^2} \right) = \ln \frac{\mu_2 \sqrt{T_2}}{\mu_1 \sqrt{T_1}}$$

is indeed striking. On closer examination, however, it appears that it

<sup>44</sup> Ghosh, Ref. 17, p. 797. By good chance, Ghosh does not use this equation for calculating  $x$  and  $\alpha$  in his tables for transition acids. The values given in these tables are consequently correct.

<sup>45</sup> Ref. 17, p. 795.

<sup>46</sup> Kendall, *J. Chem. Soc.*, 101, 1290 (1912).

<sup>47</sup> Ghosh, *ibid.*, 117, 823 (1920).

<sup>48</sup> The minus sign between the terms  $1/T_1 T_2$  and  $1/T_\infty^2$  in this equation in Ghosh's article is evidently a typographical error.

is necessary to utilize the experimental values of  $\mu$  at two temperatures  $T_1$  and  $T_2$  to evaluate  $W_0$  (the work required to free the ions of a gram-molecule at absolute zero) for each salt. The figures for  $\mu$  (calc.) and  $\mu$  (obs.) are thus made identical at two points in the temperature range, and in Ghosh's tables comparative figures for  $\mu$  are given only for from one to three other temperatures, in no case differing more than  $50^\circ$  from a fixed point. Since  $\mu$  varies regularly with the temperature,<sup>49</sup> agreement between calculated and observed values under the above conditions is almost inevitable and does not necessarily establish the validity of several new assumptions which Ghosh introduces.

Only one of these assumptions will be considered here, namely, that  $W$  is zero at the melting-point  $T_m$  or, in other words, that fused salts are completely dissociated into *free* ions. This assumption is obviously in direct opposition to the space-lattice arrangement postulated in earlier articles, since the proximity of the oppositely-charged radicals in the pure melt would certainly involve a large proportion of bound ions. It is also incompatible with the experimental results of Goodwin and Mailey,<sup>50</sup> which show that the conductivity of a fused salt mixture, when the components contain a common ion, is *less* than that computed from the law of mixtures, while in a mixture containing no common ion, where metathesis is possible, the conductivity is *greater*.

The conductivity of silver iodide at its melting point is actually less in the *fused* than in the *crystalline* state.<sup>51</sup> Fused aluminum chloride and bromide are practically non-conductors.<sup>52</sup> It is rather difficult to understand why silver bromide is a salt, but not silver iodide, or why the halides of aluminum should not be classed with those of magnesium.

**The Conductivity of Salts in Mixtures of Pyridine and Water.**—The sixth and last paper of Ghosh<sup>53</sup> compares his own experimental figures for the molecular conductivity of potassium, sodium and barium chlorides in pyridine-water mixtures at  $0^\circ$  and  $18^\circ$  with those calculated from his equations. Satisfactory agreement is again claimed but, as in the case of the same salts in water,  $\mu_p$  (obs.) and  $\mu_p$  (calc.) are made identical at a point in the centre of the dilution range, and variations in  $\mu_p$  throughout this range are in general small, so that the degree of concordance obtained is not unexpected. As the percentage of pyridine in the solvent is increased, and the proportion of free ions changes more rapidly with the dilution, significant deviations appear. In the case of the solvent containing 80% by weight of pyridine, these deviations range from 1

<sup>49</sup> Benrath and Wainoff [*Z. physik. Chem.*, 77, 257 (1911)] reproduce their experimental data very satisfactorily by the simple empirical equation:  $\log \mu = a + bT$ .

<sup>50</sup> Goodwin and Mailey, *Phys. Rev.*, 25, 469 (1907); 26, 28 (1908).

<sup>51</sup> Tubandt and Lorenz, *Z. physik. Chem.*, 87, 523 (1914).

<sup>52</sup> Isbekow and Plotnikow, *Z. anorg. Chem.*, 71, 328 (1911).

<sup>53</sup> Ref. 47, p. 1390.

to 2 units, even although the extreme variation of  $\mu_0$  from the fixed point in the center of the range is only from 2 to 5 units.

Much more striking agreement, however, is obtained by Ghosh from the data of Hartley, Thomas and Applebey<sup>54</sup> for lithium nitrate in the same mixed solvents. The dilutions tested range from  $v = 16$  to  $v = 1024$ , and  $\mu_0$  (obs.) is made identical with  $\mu_0$  (calc.) at a point *outside* this interval (namely at  $v = 8$ ). The concordance throughout the whole dilution range is exceedingly satisfactory. Even when the solvent contains from 80 to 96% by weight of pyridine, observed and calculated values agree within the limits of experimental error.

This peculiarity, remarked upon by Ghosh, is fully explained when reference is made to the original data of Hartley, Thomas and Applebey.<sup>55</sup> In only 2 cases out of a total of 32 are the values employed by Ghosh for  $\mu_0$  (obs.) identical with the figures obtained by these authors. The values for  $\mu_0$  (calc.) given by Ghosh in this table are also not derivable from his equations. The agreement arrived at is therefore entirely imaginary.

That the true experimental data of Hartley, Thomas and Applebey are not at all in accordance with the theory of Ghosh will be evident from the figures for a single pyridine-water mixture presented in Table IV below.

TABLE IV

MOLECULAR CONDUCTIVITY OF LITHIUM NITRATE IN A PYRIDINE-WATER MIXTURE CONTAINING 46.67 MOL. PER CENT. OF PYRIDINE  $T=25.08^\circ$

$v$	16	32	64	128	256	512	1024
$\mu_0$ (obs.).....	24.35	26.6	28.4	30.0	31.2	31.7	31.9
$\mu_0$ (calc.).....	25.1	28.3	31.2	33.6	35.7	37.5	39.0

The values for  $\mu_0$  (calc.) are obtained from the Ghosh equation with the use of the observed value, 21.50, for  $\mu_0$  at  $v = 8$ . For the dielectric constant of the solution the value 20.8, derived from Ghosh's own data,<sup>56</sup> is employed.

Similar discrepancies between  $\mu_0$  (obs.) and  $\mu_0$  (calc.) are found for all mixtures rich in pyridine.

**The Ionization of Salts in Solvents of Low Dielectric Constant.**—The Ghosh equation fails, indeed, to reproduce the ionization of salts not only in water-pyridine mixtures containing excess of pyridine, but in *all* solvents with a low dielectric constant. This will be obvious from a consideration of the following table, where the calculated proportions of free ions at various dilutions in solvents of various dielectric constants are shown.

<sup>54</sup> Hartley, Thomas and Applebey, *J. Chem. Soc.*, 93, 538 (1908).

<sup>55</sup> Ref. 54, p. 552.

<sup>56</sup> Ref. 47, p. 1392.

TABLE V

IONIZATION OF UNI-UNIVALENT ELECTROLYTES AT 18°, ACCORDING TO THE GHOSH THEORY

Dielectric Constant of Solvent	$\epsilon = 1$	$\epsilon = 10$	$\epsilon = 100$	$\epsilon = 1000$	$\epsilon = 10000$
1	$0.81 \times 10^{-18}$	$0.84 \times 10^{-8}$	0.00151	0.0491	0.2488
2	$0.28 \times 10^{-8}$	0.00091	0.0389	0.2215	0.4967
5	0.0024	0.0610	0.2729	0.5472	0.7580
10	0.0491	0.2468	0.5222	0.7399	0.8694
20	0.2215	0.4967	0.7228	0.8601	0.9324
50	0.5472	0.7560	0.8782	0.9415	0.9724
100	0.7399	0.8694	0.9371	0.9703	0.9864

The most important point disclosed by the above figures is that, in solvents of low dielectric constant, the ionization of salts should, according to the Ghosh theory, increase *exceedingly rapidly* with the dilution. Where the dielectric constant is very low, the variation demanded is so extreme that even the *specific conductivity* should increase with the dilution. For example, in chloroform, with a dielectric constant of 5, the specific conductivity of a 0.01 *N* solution of a uni-univalent salt should exceed slightly that of a 1.0 *N* solution. In benzene, with a dielectric constant a little above 2, the specific conductivity of a 0.01 *N* solution should be several hundred times larger than that of a 1.0 *N* solution. Even this figure sinks into insignificance when compared with the wonderful results that should be obtained for the conductivity of air (with a dielectric constant very little in excess of 1) containing a small amount of vapor from a volatile salt.

In practice, of course, we do not find the specific conductivity of salts in solvents of low dielectric constant increasing in this remarkable way. Exactly the opposite behavior is exhibited; it is a general rule that the specific conductivity decreases so rapidly throughout the range 1.0 *N* to 0.01 *N* that even the *equivalent conductivity* decreases. That this abnormality is characteristic for salts in solvents of low dielectric constant, and that it is more marked the smaller the dielectric constant, has been conclusively shown by Sachanov.<sup>57</sup>

Another point may now be noted. The theory of Ghosh requires that salts of the same type should be ionized to the same extent in the same solvent at any given dilution. In an earlier section of this paper the validity of this rule for uni-univalent salts in aqueous solution was questioned, but no definite conclusion reached. For the same salts in non-aqueous solutions, however, the rule is obviously not valid. From the many cases found in the literature a single example, the lithium halides in pyridine,<sup>58</sup>

<sup>57</sup> Sachanov, *Z. physik. Chem.*, 80, 13 (1912); 83, 129 (1913).

<sup>58</sup> Anderson, *J. Phys. Chem.*, 19, 753 (1915).

may be cited. At  $25^{\circ}$  and  $v = 10$ , the equivalent conductivities are as follows: lithium chloride, 0.322; lithium bromide, 5.34; lithium iodide, 23.35. The abnormal tendency of iodides towards polymerization<sup>60</sup> cannot be adduced to explain these figures, since it is the *iodide* which here behaves normally.

Before we sum up the results of our examination of the theory of Ghosh, two lines of evidence which have been brought forward in recent papers by other investigators in support of the hypothesis that strong electrolytes are completely dissociated in aqueous solution may be briefly discussed.

**The Distribution of a Salt between an Ionizing and a Non-ionizing Solvent.**—Silver perchlorate is a salt which is fairly soluble in benzene, giving a solution which is practically non-conducting. The extraction of the salt from its benzene solution by water is quantitatively complete. It follows that no molecular species is common to the two liquid layers, and the conclusion has been drawn that the salt, in the water layer, is entirely dissociated.<sup>60</sup>

If this conclusion is generally valid, then *any* strong electrolyte should be completely extracted from a non-ionizing solvent by water. Hantzsch<sup>61</sup> has found, indeed, that dimethyl-ammonium chloride is almost totally removed from its solution in chloroform by shaking with water. Opposite results, however, have been obtained by Wedekind and Paschke<sup>62</sup> with the system propylbenzylmethylphenyl-ammonium bromide:chloroform:water, and by Drucker<sup>63</sup> with 3 systems of the type tribenzylammonium bromide:bromoform:water. In all these cases it has been established that the distribution of the salt between the two solvents follows the laws formulated by Nernst on the basis of the Arrhenius ionization theory.

The bulk of the evidence in this field, therefore, is *against* the hypothesis of complete ionization. In both instances where practically complete extraction has been claimed, the solubility ratio is already overwhelmingly in favor of the water. Thus, in the experiments of Hill, the calculated distribution ratio of silver perchlorate between water and benzene is 406 to 1. While the ratio actually obtained was far in excess of this, yet it is obvious that more convincing proof would be afforded if a salt with a smaller solubility ratio could be similarly extracted.

**The Vapor Pressure of the Hydrogen Halides in Aqueous Solution.**—The fact that a normal solution of hydrochloric acid does not have an appreciable vapor pressure of hydrogen chloride, although according to

<sup>60</sup> Ghosh, Ref. 17, p. 630.

<sup>61</sup> Hill, *THIS JOURNAL*, 43, 254 (1921).

<sup>62</sup> Hantzsch, *Zentr.*, [2] 1902, p. 922; *Ber.*, 38, 1046 (1906).

<sup>63</sup> Wedekind and Paschke, *Z. physik. Chem.*, 73, 118 (1910).

<sup>64</sup> Drucker, *Z. Elektrochem.*, 18, 562 (1912).

the Arrhenius theory 15% of the solute must be assumed to be in the unionized state, has been cited by Noyes and MacInnes<sup>64</sup> as another point in favor of the complete dissociation hypothesis.

An alternative explanation of this phenomenon, however, is available. The hydrogen halides, like all strong acids,<sup>65</sup> are very extensively hydrated in aqueous solution, and the lack of an appreciable vapor pressure may very well be due to the practically complete combination of volatile HCl molecules with the solvent to form non-volatile complexes of the type  $\text{HCl} \cdot x\text{H}_2\text{O}$ .

The consideration of an analogous case may assist in deciding the relative plausibilities of the two explanations. A normal solution of water in 100% sulfuric acid resembles exactly a normal solution of a hydrogen halide in water. It is a good conductor of electricity,<sup>66</sup> and possesses practically zero vapor pressure of the volatile solute. Are we to conclude that water, dissolved in sulfuric acid, is entirely dissociated into  $\text{H}^+$  and  $\text{OH}^-$ ?

**The Role of the Solvent in Ionization.**—This brings us to the vital question of the part played by the solvent in ionization. Both the Arrhenius theory and the theory of complete ionization, as at present developed, refer conductance in solution entirely to the solute. The solvent is either regarded as so much "dead space," in which the solute has opportunity to dissociate, or its activity is restricted to the formation of "ionic envelopes." Detailed arguments against this point of view have been presented in previous papers,<sup>67</sup> in which the essential equivalence of solvent and solute has been made the fundamental feature of a modified ionization theory. Any hypothesis which neglects one component altogether is bound to give a distorted outlook upon the subject and to lead to inconsistent conclusions.

Such inconsistencies, indeed, are immediately evident when we try to extend the current hypotheses, which are based almost entirely upon the behavior of dilute aqueous solutions, to conducting solutions in general. Ethyl alcohol is held to be a typical non-electrolyte, not broken up at all into ions; formic acid a typical weak electrolyte, only slightly dissociated in solution; hydrogen chloride a typical strong electrolyte, extensively (or wholly) dissociated in solution. These distinctions have

<sup>64</sup> Noyes and MacInnes, Ref. 6, p. 245. MacInnes, *THIS JOURNAL*, **43**, 1225 (1921). The discussion of other points adduced in support of the theory of complete dissociation, particularly the interpretation of electromotive-force measurements and the vexing question of the abnormal activity of undissociated molecules, will be taken up in a subsequent article.

<sup>65</sup> See Kendall, Booge and Andrews, *THIS JOURNAL*, **39**, 2307 (1917).

<sup>66</sup> Walden, *Trans. Faraday Soc.*, **6**, 71 (1910).

<sup>67</sup> See, particularly, Kendall and Booge, *THIS JOURNAL*, **39**, 2323 (1917). Kendall and Gross, *ibid.*, **43**, 1416 (1921). Kendall, *Proc. Nat. Acad. Sci.*, **7**, 56 (1921).



no basis in fact, and have been drawn simply because we have allowed our aqueous environment to mislead us. If we worked in a world where formic acid was the standard reference liquid, ethyl alcohol, water and hydrogen chloride would all appear to be weak electrolytes. In a universe where trichloro-acetic acid was the common solvent, water would become a typical strong electrolyte and hydrogen chloride a practically non-ionized substance.

Our division of substances into strong, transition, weak and non-electrolytes (or into polar and non-polar compounds) is therefore in many cases purely arbitrary. This may be emphasized by attempting to fix definite limits for any particular class. Naphthalene- $\beta$ -sulfonic acid, according to Ghosh,<sup>68</sup> resembles hydrogen chloride in being entirely dissociated in water solution; trichlorobutyric acid, however, is a "transition acid" and gives both undissociated molecules and ions. Where are we to draw the line between *transition* and *strong* electrolytes?<sup>69</sup> How long, also, will a strong electrolyte remain "completely ionized" as the dielectric constant of the solvent is gradually decreased? Hill considers silver perchlorate to be entirely non-ionized in benzene and entirely ionized in water; what would be its character in a solvent of intermediate type? Ghosh, on the other hand, regards the ionization of strong electrolytes in solvents of low dielectric constant to be still complete, but the limit must evidently be reached before the dielectric constant approximates to unity, since otherwise hydrogen chloride diluted with dry air should be an excellent conductor of electricity.<sup>70</sup>

The "strength of an electrolyte" or the "polarity of a compound" depends primarily, as has been shown experimentally in preceding articles,<sup>71</sup> upon its ability to form ionically unstable complexes with the solvent selected. The most serious objection, therefore, to the theory of Ghosh is that it ignores entirely the part played by the solvent in the ionization process.

**Conclusions.**—The nature of the results obtained from our detailed examination of Ghosh's articles renders extended comment superfluous. It is clear that the equations employed by Ghosh are not, in general, in satisfactory agreement with the experimental facts. In certain cases they serve very well as interpolation equations over a restricted range, but confirmatory evidence as to their fundamental validity is totally lacking. It may be noted that the application of the corrections discussed in the earlier sections of this paper would not materially affect this conclusion.

<sup>68</sup> Ref. 17, p. 794.

<sup>69</sup> Compare Dawson, *Trans. Faraday Soc.*, 15, 152 (1919).

<sup>70</sup> See Table V, p. 733.

<sup>71</sup> See, particularly, Kendall and Gross, *THIS JOURNAL*, 43, 1426 (1921).

It has not, of course, been proved hereby that the whole theory of Ghosh is invalid. The abnormality of strong electrolytes cannot possibly be accounted for on a purely kinetic basis, and the necessity of taking into consideration the electrical forces exerted between the various species (molecular or ionic) existent in a conducting solution cannot be ignored. This idea, however, is not original with Ghosh; it has been brought forward by several previous investigators, notably by Noyes.<sup>73</sup> Ghosh carries it too far in one respect, namely, in regarding the electrical forces as all-important and neglecting all other factors entirely. In another respect he does not carry it far enough, namely, in restricting the electrical forces to solute particles and disregarding the polarity of the solvent.

In the absence of any evidence in its favor, Ghosh's second postulate—the space-lattice arrangement of the charged solute particles in definite mean positions in the solution—cannot be considered as more than an interesting possibility. While it cannot be definitely disproved, the behavior of salts in solvents of low dielectric constant argues very strongly against it. For the present, it is certain that no arguments have been adduced which would justify us in discarding entirely our present kinetic interpretation of the state of affairs in conducting solutions. The ionization theory of Arrhenius may be in need of modification, but no case has yet been made out for its abandonment.

### Summary

A critical analysis of the ionization theory of Ghosh has led to the following conclusions.

1. The second and third postulates are inconsistent. If the particles of a salt in solution possess a definite space-lattice arrangement, as in the crystalline state, then the combination of 2 oppositely charged particles to form a salt-molecule or a completely saturated electrical doublet is impossible.

2. Ghosh's calculation of the electrical work required to separate the component radicals of a gram-molecule of dissolved salt is erroneous. The value actually derived, assuming a cubic space-lattice arrangement, exceeds that obtained by Ghosh by 75%.

3. The experimental conductivity data for potassium chloride solutions are not in agreement with the equation which Ghosh obtains from his postulates, or with various corrected forms of this equation.

4. The agreement claimed by Ghosh to exist between his equations and the experimental results of previous investigators is largely fictitious. The remarkable coincidence of calculated and observed values in many tables is due to far too frequent errors of calculation and transcription.

<sup>73</sup> Noyes, *THIS JOURNAL*, 30, 351 (1908).

In other cases, the only legitimate deduction is that the equations tested serve very well as interpolation equations over a restricted range.

5. No confirmation of the theory of Ghosh is afforded by the experimental data for (a) the variation of equivalent conductivity with dilution for salts in aqueous solution, (b) the temperature coefficient of the ratio  $\mu_0/\mu_\infty$ , (c) the electrical conductivity of non-aqueous solutions, (d) the molecular number  $i$  and the Clausius theorem, (e) the ionization of strong acids, (f) the ionization of weak acids, (g) the ionization of transition acids, (h) the electrical conductivity of pure salts in the solid and fused states, (i) the conductivity of salts in mixtures of pyridine and water, (j) the ionization of salts in solvents of low dielectric constant, (k) the distribution of a salt between an ionizing and a non-ionizing solvent, (l) the vapor pressure of the hydrogen halides in aqueous solution.

6. The rôle of the solvent in ionization, which is ignored altogether by Ghosh, must be taken into account in any complete theory of conducting solutions.

7. In its present form, the ionization hypothesis of Ghosh is unacceptable, and certain of the postulates upon which it is based must be either modified or rejected.

NEW YORK, N. Y.

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[CONTRIBUTION FROM THE RESEARCH DIVISION OF THE CHEMICAL WARFARE SERVICE,  
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## THE PREFERENTIAL CATALYTIC COMBUSTION OF CARBON MONOXIDE IN HYDROGEN\*

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An important factor in the commercial success of the Haber process for the synthesis of ammonia is the cost of the pure hydrogen which it requires. At present this hydrogen is usually obtained by "converting" mixed water- and producer- gas using a considerable excess of steam and a suitable catalyst, into a mixture relatively rich in hydrogen and carbon dioxide, and poor in carbon monoxide. The carbon dioxide is then largely removed by a thorough water-scrubbing under moderate pressures. The compositions of these gaseous mixtures are as follows, according to R. S. Tour.<sup>1</sup>

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<sup>1</sup> Tour, *J. Ind. Eng. Chem.*, 12, 844 (1920).

	After conversion %	After water-scrubbing %
H <sub>2</sub> .....	52-52	73-72
N <sub>2</sub> .....	17-17	24-23
CO <sub>2</sub> .....	29-27	0.1-1.0
CO.....	2-4	3-5
X.....	0.4-0.8	0.5-1.0

where X = argon, methane, etc.

To remove the 3 to 5% of carbon monoxide remaining in the gaseous mixture after the water-scrubbing, the practice has been to scrub thoroughly under high pressure with ammoniacal solutions of cuprous salts. By this means the carbon monoxide content can be reduced to between 0.1 and 0.01%. This degree of purity may be adequate, but the process is difficult and costly. It is desirable therefore, if possible, to devise one which is simpler and more economical.

With this requirement in mind, we have investigated the behavior of an absorbent for carbon monoxide called Hopcalite, developed during the war by the U. S. Bureau of Mines and the Chemical Warfare Service of the U. S. Army.<sup>2</sup> This material, consisting of a mixture of metallic oxides, is not strictly speaking an absorbent, for it operates by burning the carbon monoxide catalytically at the expense of the oxygen of the air; and if the air is adequately dried, it is not itself altered in the process. If this material should prove to be unaffected by hydrogen under any feasible conditions at which it would catalytically oxidize carbon monoxide, there appears to be the possibility of a cheap and simple method for the removal of carbon monoxide from the above mentioned mixture.

There is a good deal of evidence in the literature that as a rule easily reducible oxides are reduced at lower temperatures by carbon monoxide than by hydrogen. Thus, Campbell<sup>3</sup> found for a specially prepared copper oxide, and Wright and Luff<sup>4</sup> for different varieties of the various oxides of copper, iron, manganese, lead, nickel, and cobalt, initial temperatures of reduction averaging about 60° lower for carbon monoxide than for hydrogen. Fay, Southerland and Ferguson<sup>5</sup> obtained similar results with the oxides listed in the following table.

TABLE I  
INITIAL TEMPERATURES OF REDUCTION

Oxide	With CO °C.	With H <sub>2</sub> °C.	Oxide	With CO °C.	With H <sub>2</sub> °C.
Au <sub>2</sub> O <sub>3</sub> .....	0	0	HgO red.....	90	125
Ag <sub>2</sub> O.....	0	0	CdO.....	140	125
Hg <sub>2</sub> O.....	0	80	CrO <sub>3</sub> .....	95-100	140-150
HgO yellow.....	0	50			

<sup>2</sup> Lamb, Bray and Frazer, *J. Ind. Eng. Chem.*, 12, 213 (1920).

<sup>3</sup> Campbell, *Am. Chem. J.*, 17, 688 (1895).

<sup>4</sup> Wright and Luff, *J. Chem. Soc.*, 33, 1, 504 (1878).

<sup>5</sup> Fay, Southerland and Ferguson, *Poly. Engineering*, 10, 72 (1910).

It seemed not unlikely, therefore, that Hopcalite would also require a higher temperature to react with hydrogen than with carbon monoxide, and that a range of temperatures would exist in which carbon monoxide might be completely and rapidly oxidized, while hydrogen would be unaffected. We have therefore studied the behavior of Hopcalite toward both dry and moist mixtures of hydrogen and air, of carbon monoxide and air, and of hydrogen and carbon monoxide and air.

### Behavior of Hopcalite toward a Dry Mixture of Hydrogen and Air

We first tried the behavior of Hopcalite at room temperature toward a dry mixture of 90% hydrogen and 10% air.<sup>6</sup> The Hopcalite was contained in a glass tube of 3 sq. cm. cross section in a layer 5 cm. deep. The glass tube was surrounded by a larger glass tube wound with a spiral of Nichrome ribbon which could be electrically heated. A thermometer was fitted into the inner tube with its bulb just above the catalyst. The affluent gas mixture passing up through the narrow annular space between the two tubes was preheated, and then passed downward through the catalyst. The gas mixture was prepared by mixing hydrogen from a pressure cylinder in the proper proportions with air from a gasometer by means of flowmeters, and drawing this mixture through a third flowmeter, through bead drying towers containing sulfuric acid, and thence leading it into the catalyst tube. A rate of flow of 1500 cc. per minute was adopted, corresponding to a space velocity of 6000 per hour.<sup>7</sup> Under these conditions after a half hour's running no warming of the Hopcalite occurred, and hence no considerable oxidation of hydrogen could have taken place. When, however, the temperature of the affluent gases was raised to about 60° or 70° rapid oxidation of the hydrogen set in, and the catalyst became incandescent. Since

<sup>6</sup> The Hopcalite catalyst used in this investigation was prepared in the small experimental plant at the American University [for full details see Merrill and Scalione, *THIS JOURNAL*, 43, 1982 (1921)]. It was a 2-component mixture consisting of 60% of  $MnO_2$  and 40% of  $CuO$ , primarily designed for a carbon monoxide absorbent or catalyst for gas-mask canisters. All precipitations were carried out in iron containers; but the precipitates were washed in wooden tanks by decantation, ordinary tap water being used.

The preparation of each component of the Hopcalite mixture was as follows. The manganese dioxide was prepared from manganous sulfate and potassium permanganate in strong sulfuric acid solution, the first step being the formation of  $Mn(SO_4)_2$ . On dilution the  $Mn(SO_4)_2$  is hydrolyzed to  $MnO_2$  giving a very finely divided precipitate which is extremely satisfactory as a component in this catalytic absorbent. The  $MnO_2$  was activated by mixing with it 40% of cupric oxide prepared from basic copper carbonate. After the thorough mixing of these two thoroughly washed pulps in a kneader and compression of the mixture under 6000 lbs. per sq. inch, the pressed cake was dried at 120–130°, crushed to the desired mesh (in these experiments 10–16), screened, and redried for 3 hours at 200°.

<sup>7</sup> *I. e.*, 6000 liters per liter of catalyst per hour,

Hopcalite oxidizes carbon monoxide catalytically under these conditions, at temperatures of  $0^{\circ}$  and lower,<sup>3</sup> this experiment indicates that it should be possible to oxidize carbon monoxide preferentially in the presence of a large excess of hydrogen at room temperature, provided there is no induction effect of the burning carbon monoxide on the hydrogen.

### Behavior of Hopcalite toward a Dry Mixture of Hydrogen, Carbon Monoxide and Air

To test the above conclusions, a mixture of 89.5% of hydrogen, 0.5% of carbon monoxide and 10% of air was dried and passed through the catalyst at a space velocity of 6000 per hour, and provision made to detect any water formed or carbon monoxide remaining unburned. The procedure was as follows.

Hydrogen prepared from zinc and hydrochloric acid, and purified from arsine and phosphine, was mixed in a large gasometer with the required proportions of air and of carbon monoxide prepared from formic acid. From this the gas mixture passed through 2 bead towers charged with sulfuric acid, through a flowmeter, and then into an unjacketed glass tube of 1 sq. cm. cross section containing the catalyst. Issuing from this, it passed through a weighed U-tube containing phosphorus pentoxide, through bead towers containing a solution of potassium hydroxide, and then through 2 Gomberg bulbs charged with a solution of barium hydroxide to indicate the completeness of the removal of the carbon dioxide. The gases were now led through a quartz tube filled with copper turnings and heated electrically to  $300^{\circ}$ , in order to oxidize any carbon monoxide not burned in the catalyst; through 2 more Gomberg bulbs containing barium hydroxide solution, and finally through the rotary oil pump to waste. A rate of flow of 500 cc. per minute corresponding to a space velocity of 6000 per hour was maintained. The experiment was continued for 1 hour, but no increase in weight of the phosphorus pentoxide tube occurred, nor was there any test for carbon dioxide in the final Gomberg bulb. The experiment was repeated several times with other samples of Hopcalite, with identical results. This demonstrates that the carbon monoxide is completely burned under these conditions, and that no more than a trace of hydrogen can have been oxidized.<sup>3</sup>

The same experiment was now tried with a gas mixture of similar composition except that it contained 1% of carbon monoxide. The reaction proceeded smoothly for 7 minutes, whereupon the Hopcalite became incandescent. Considerable moisture deposited on the walls of the catalyst tube and collected in the phosphorus pentoxide tube. The experiment was repeated several times with different samples of Hopcalite with the same result.

These experiments indicate that with 1% carbon monoxide the heat of reaction is so considerable that oxidation of the hydrogen begins and a rapid incandescence follows.

<sup>3</sup> It does not demonstrate that *no* hydrogen burned, for we know that the Hopcalite is decidedly hygroscopic, and traces of moisture, if formed, might have been retained in it. However, since no decrease in its efficiency occurred, no more than a few cg. of water could have been formed with the small amount of catalyst used, and this would correspond to a ratio of less than 1:100 between the amount of hydrogen and carbon monoxide burned.

### Behavior of Hopcalite toward a Moist Mixture of Hydrogen and Air

The actual gases to be purified in the manufacture of hydrogen from water-gas are saturated with water at a temperature of perhaps 30°, and it is desirable to remove the carbon monoxide from this mixture if possible without drying. The behavior of Hopcalite toward moist mixtures of hydrogen and air was therefore tried.

In order to detect the first trace of action with greater certainty than in the former experiments a different type of catalyst tube was employed. It consisted of 3 concentric metal tubes. The inner one of about 2 sq. cm. cross section served as a cooling tube, and water could be circulated through it. The intermediate tube was of about 5 sq. cm. cross section, and the catalyst was contained in a layer 5 cm. deep in the annular space between it and the inner tube. In the catalyst were placed 4 thermocouples at different depths. As they were sensitive to less than 1° the slightest oxidation of hydrogen would be disclosed. The outer tube had a cross section of about 9 sq. cm. and was wound with Nichrome ribbon which could be heated electrically. The gas mixture was humidified by passing through 2 bead towers in series into which water was kept slowly dropping, inserted in the place of the final drying towers. These 2 towers and the catalyst tube were placed in a large electrically heated, stirred, and regulated air thermostat which maintained a temperature of  $40^{\circ} \pm 0.1^{\circ}$ , and was provided with ample shields and deflectors to eliminate any irregularities of temperature due to radiation from the incandescent lamp heater. By this means an aqueous tension of 50 mm. of mercury was imparted to the affluent gas. This gas entered the catalyst tube at the top of the annular space, and as this was rather long, was thereby somewhat preheated.

Several determinations with this apparatus at a space velocity of 6000 per hour and with mixtures of 90% hydrogen with 10% air and 1% hydrogen in 99% air showed that with this amount of water vapor present no considerable oxidation of the hydrogen occurred until a temperature of 125° was reached in the catalyst.

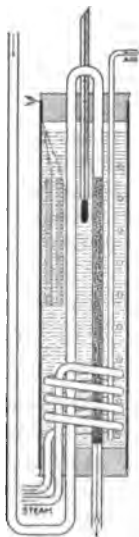


Fig. 1.

### Behavior of Hopcalite toward a Moist Mixture of Carbon Monoxide and Air

Careful experiments were now made to ascertain the temperature required for complete combustion of carbon monoxide in nitrogen, in the presence of oxygen and similar amounts of water vapor. A still more carefully designed reaction tube shown in Fig. 1 was used for this purpose.

It consisted of 2 copper tubes 7 by 400 mm. running vertically through a water-bath. The gas passed up through one of them which was empty and served as a preheater, and down through the other which was filled for a distance of about 30 cm. along its middle with 15 cc. of catalyst. The water was heated nearly to the desired temperature by means of a small coil of copper steam-pipe, and the finer regulation obtained by an electrically heated coil of Nichrome wire immersed in the bath. The bath was stirred by means of air. The same humidity towers and air thermostat as described above were used. The two gas mixtures studied contained, before humidification, 0.5% of carbon monoxide, 2.5% of air, 97% of nitrogen; and 1.0% carbon monoxide, 5% of air, 94% of nitrogen; affording in each case twice the theoretical

amount of oxygen required for the combustion of the carbon monoxide. A space velocity of 6000 per hour was maintained.

TABLE II

PERCENTAGE EFFICIENCY OF HOPCALITE IN OXIDIZING CARBON MONOXIDE IN GAS MIXTURES CONTAINING  $H_2O$  AT A PRESSURE OF 50 MM. OF MERCURY

0.5% of CO, 0.5% of $O_2$ , 99% of $N_2$		1% of CO, 1% of $O_2$ , 98% of $N_2$	
Temperature °C.	Efficiency %	Temperature °C.	Efficiency %
45	9.0	45	5.5
60	15.0	60	12.5
70	25.6	70	30.0
80	47.0	80	70.0
90	76.0	90	100.0
95	92.8	..	...
98	99.1	..	...

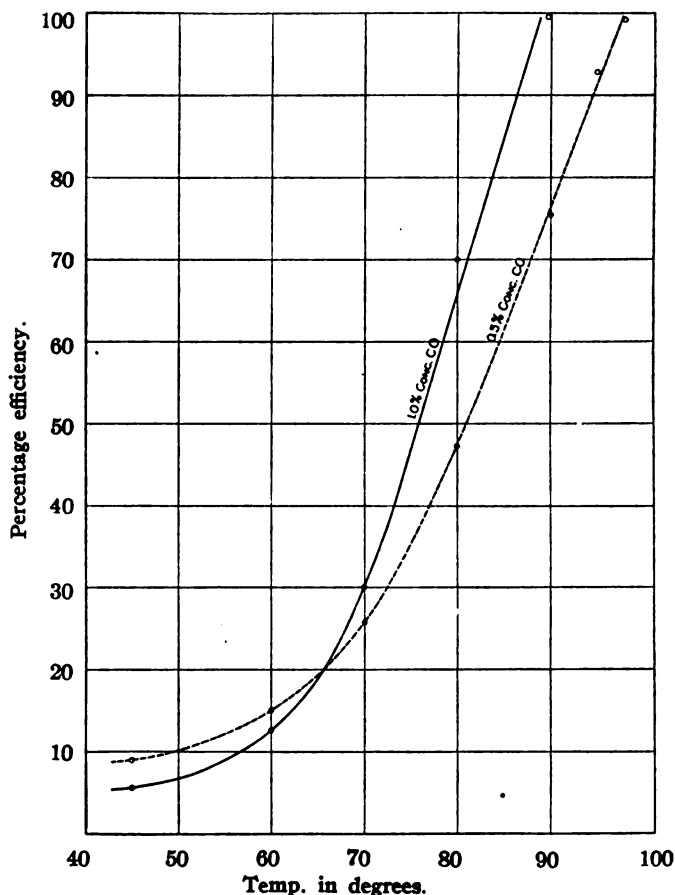


Fig. 2.—Temperature-efficiency curve.



Determinations were made by adjusting the bath to a constant temperature, passing the gas mixture through the catalyst, and determining the unburned carbon monoxide by means of the calorimetric method.<sup>9</sup> Sufficient time was allowed to insure the establishment of equilibrium conditions of constant efficiency. The results are collected in Table II, and are shown graphically in Fig. 2.

These results were confirmed by many additional measurements. They indicate that at a temperature of 90–100° in air complete oxidation of carbon monoxide is obtained even in the presence of water vapor equivalent to 50 mm. of mercury pressure, and with a relatively small excess of oxygen (100%); and that, therefore, a margin of about 20° exists between this temperature and that at which hydrogen begins to be oxidized under similar conditions.

### Behavior of Hopcalite Toward a Moist Mixture of Carbon Monoxide and Hydrogen Containing a Little Oxygen

It remained to find out whether this margin of 20° between the temperatures of oxidation of the separate gases would persist in a mixture of the two gases, or in other words, whether or not the oxidation of the carbon monoxide exerted any induction effect upon the oxidation of the hydrogen.

To do this, and at the same time to show that no serious deterioration of the catalyst occurs on prolonged running even at efficiencies less than 100%, a prolonged continuous test was carried out on a gaseous mixture containing a little carbon monoxide and oxygen and a large amount of hydrogen.

**Determination of Carbon Monoxide in the Presence of Hydrogen.**—The above mentioned calorimetric method so useful for the analysis of carbon monoxide in air could not be used here on account of the relatively large amount of hydrogen present. A complete combustion of the gas, on the other hand presented numerous difficulties. We attempted to apply the iodine pentoxide method which has been recommended for this purpose,<sup>10</sup> but without success. We found that at 150–160° iodine pentoxide oxidizes about 15% of the hydrogen in a 1 or 10% hydrogen-air mixture, and 26% of the hydrogen in a 10% hydrogen, 0.9% carbon monoxide, and 89.1% air mixture. At 96–100° only about 2.6% of the hydrogen of a 10% hydrogen-air mixture was oxidized, but with 1% carbon monoxide over 90.5% and 96.5% was oxidized at this temperature in two determinations. This greater activity of our iodine pentoxide may have been due to its preparation by the chloric acid method.<sup>11</sup>

Finally, since we had already demonstrated that Hopcalite oxidizes carbon monoxide completely at room temperature in dry hydrogen containing a little oxygen, we simply dried the effluent gas, passed it through a layer of this substance, and collected the carbon dioxide in standard alkali. There were, however, two difficulties which required consideration. In the first place, it was found that Hopcalite retains adsorbed carbon dioxide tenaciously at room temperature. The adsorbed carbon dioxide is given off slowly at 100°, and more rapidly at 140° (boiling xylene), while at 205° (boiling nitro-

<sup>9</sup> Lamb and Larson, *THIS JOURNAL*, 41, 1908 (1919).

<sup>10</sup> Nicloux, *Compt. rend.*, 126, 746 (1898). Kinnicut and Sanford, *THIS JOURNAL*, 22, 14 (1900). Graham and Winhill, *J. Chem. Soc.*, 105, 1996 (1914). Graham, *J. Soc. Chem. Ind.*, 38, [2] 10 (1919).

<sup>11</sup> Lamb, Bray and Geldard, *THIS JOURNAL*, 42, 1636 (1920).

benzene) carbon dioxide of constitution is apparently given off slowly from the basic carbonates in the Hopcalite, for prolonged heating to  $240^{\circ}$  failed to eliminate it completely. After use, therefore, the Hopcalite was first swept out at room temperature with air, and then heated, and the sweeping continued. The length of time necessary for complete removal varies with the amount of carbon dioxide adsorbed, the quantity of Hopcalite used and the velocity of the air current, but in our experiments 45 minutes was found to be adequate. The second difficulty was the complete absorption of the carbon dioxide in the dilute alkali from such relatively dilute mixtures (0.5 to 0.02% of carbon monoxide) at rapid rates of flow. This was successfully accomplished by using 3 small absorption bulbs of the injector type arranged in series, and heated to about  $80^{\circ}$  in a bath of water. A centrifugal stirrer-injector would probably be even more efficient. From the point of view of the difficulty of absorption the retention of the carbon dioxide by the Hopcalite is an advantage, for particularly at low concentrations it is practically all adsorbed, and can then be driven out by a slow current of air at a considerably higher concentration. The procedure adopted, therefore, is as follows. The sample of gas, varying in volume from 2 liters when about 0.5% of carbon monoxide is present to 10 liters when less than 0.02% of carbon monoxide is present, is mixed with about  $\frac{1}{2}$  of its volume of purified air, unless it already contains a considerable excess of oxygen. It is then passed through bead towers moistened with potassium hydroxide solution, another bead tower moistened with sulfuric acid, thence into the oxidation apparatus, and finally through the absorption bulbs, at a rate of about 300–500 cc. per minute. Pure air is then passed through the apparatus until the gas therein has been displaced. Finally the xylene is heated to boiling, and a current of pure air, quite slow at first but finally increasing in amount to about 300 cc. per minute, is passed through the apparatus for about 45 minutes. The absorption bulbs are then disconnected, washed out with water free from carbon dioxide, and the liquid titrated with dilute standard acid (about 0.02 *N*), using phenolphthalein as indicator. Blank determinations are also run and the correction, seldom amounting to as much as 0.001%, is applied.

Results obtained on known mixtures, varying between 0.5% and 0.005% of carbon dioxide, gave a satisfactory concordance. Thus, with the very dilute mixtures given in the following table the inaccuracy amounts to but 0.0015 and 0.0006%, respectively.

TABLE III  
ANALYSIS OF CARBON MONOXIDE-HYDROGEN MIXTURE  
Concentrations of carbon monoxide

Taken %	Found %	Corrected %	Error %
0.0110	0.0102	0.0095	-0.0015
0.0055	0.0056	0.0049	-0.0006

**Continuous Test.**—The composition of the gaseous mixture was 74.25% of hydrogen, 24.75% of nitrogen, 0.5% of carbon monoxide, and 0.5% of oxygen. To prepare this mixture the carbon monoxide and oxygen were first mixed in equal volumes and stored in 20-liter glass aspirator bottles, and then fed into the mixing chamber through a flowmeter at the rate of 5 cc. per minute. A very pure mixture of hydrogen and nitrogen in the proportion of 3:1 at a pressure of 100 atmospheres was kindly furnished us by the Arlington Laboratory of the Nitrate Division of Ordnance, U. S. A. It had been prepared by cracking ammonia gas at a high temperature, and was further purified by passage through a deep layer of Hopcalite, through a tower containing chromic acid maintained at

80°, and finally through another containing 50% sodium hydroxide solution. Thence it entered a constant-pressure tube where a continuous slight escape of the excess gas took place, and then entered a mixing chamber where it mingled with the carbon monoxide-air mixture, the resulting mixture being sucked through a second flowmeter, the humidity towers and finally through the catalyst tube and the analytical train. The catalyst tube consisted of a copper tube 7 mm. wide and 400 mm. long to which a spiral coil of small copper tubing was soldered to serve as a preheater. The Hopcalite occupied about 10 cm. length of the copper tube, and was supported by a small roll of copper gauze. The tube and preheater were immersed in a paraffin thermostat electrically heated and regulated to maintain a temperature of  $101.8^\circ \pm 0.2^\circ$ .

With these arrangements the gas mixture was now drawn through the apparatus at a rate of 500 cc. per minute, corresponding to a space velocity of 6000 per hour with the 5 cc. of catalyst employed, and the effluent gas analyzed at frequent intervals for carbon monoxide by the method outlined above. With this small volume of catalyst a fairly constant efficiency of 93% was maintained for a continuous operation of 200 hours. During this period the catalyst purified 6000 liters of gas, or over a million times its own volume, and removed nearly 10 times its own weight of carbon monoxide without deterioration.

During the succeeding 48 hours the efficiency slowly dropped to 74%, when the run was discontinued and the catalyst tube opened. It was found that the top (initial) layer of catalyst had darkened in color and a further examination showed that paraffin had leaked in through 2 pinholes just below the level of the paraffin bath. This was adequate to explain the drop in efficiency in the concluding 48 hours.

Experiments somewhat similar to the above were carried out with a mixture containing 1% of carbon monoxide, 10% of air, 29% of nitrogen, and 60% of hydrogen, but after a short period of operation incandescence of the catalyst took place, indicating, as in the case of dry hydrogen, that the heat of reaction is not dissipated in our apparatus rapidly enough to prevent reaction with the hydrogen.

### **The Influence of Various Factors on the Efficiency of the Hopcalite and the Temperature Rise in the Catalyst**

Having shown that 0.5% carbon monoxide can be successfully removed even from a very moist mixture of hydrogen and nitrogen, it remained to investigate the influence of important factors such as space velocity at different temperatures, catalytic poisons, and the concentration of the oxygen, on the catalytic combustion of the carbon monoxide. Moreover, since the rate of dissipation of the heat of reaction from the catalyst limits the concentration of carbon monoxide which can be tolerated by

the catalyst in the presence of hydrogen, we have on the one hand considered means for combating this effect and on the other have studied the actual temperatures produced in tubes of different diameters at a variety of space velocities.

**Temperature and Space Velocity.**—The variation with the temperature of the efficiency of the catalytic oxidation of 0.5% and 1% carbon monoxide in a mixture of moist oxygen and nitrogen at a space velocity of 6000 per hour had already been studied as described above (pp. 742–744). We now made similar measurements at space velocities up to 30,000 and in tubes 4 to 7 mm. in diameter, with otherwise the same apparatus. The results are collected in Table IV, and are shown graphically in Figs. 3 and 4. The temperatures were those of the well-stirred water-bath; the temperatures within the catalyst were undoubtedly somewhat higher.

TABLE IV

EFFECT OF SPACE VELOCITY, TEMPERATURE, ETC., ON THE EFFICIENCY OF OXIDATION OF CARBON MONOXIDE BY HOPCALITE

20% of oxygen, 79.5% of nitrogen and 0.5% of carbon monoxide used in all experiments except those marked (a) in which 79% of nitrogen and 1.0% of carbon monoxide were used.

Temp. bath °C.	CO oxidized %	Temp. bath °C.	CO oxidized %	Temp. bath °C.	CO oxidized %
Space velocity 6000		Space velocity 18000		Space velocity 27000	
50 mm. of H <sub>2</sub> O. Tube 5.5 mm.		No H <sub>2</sub> O. Tube 4 mm.		50 mm. of H <sub>2</sub> O. Tube 4 mm.	
71	59	29	64	85	51
80	90	40	86	95	80
87	99	50	94	99	90
Space velocity 13000		61	99	105	95
50 mm. of H <sub>2</sub> O. Tube 4 mm.		70	100	110	98
72	41	Space velocity 18000		113	100
80	61	50 mm. of H <sub>2</sub> O. Tube 4 mm.		Space velocity 30000	
85	79	80	41	50 mm. of H <sub>2</sub> O. Tube 5.5 mm.	
90	88.5	85	54	77	33
95	94.5	85	58 <sup>b</sup>	80	37
99	98	90	69	84	50
Space velocity 15000		95	86	90	60
50 mm. of H <sub>2</sub> O. Tube 5.5 mm.		99	95	99	83
80	57	105	99	99	81 <sup>a</sup>
80	61 <sup>a</sup>	107	100	Space velocity 30000	
		85	58	No H <sub>2</sub> O. Tube 4 mm.	
				54	61
				65	80
				72	88
				85	98.5
				90	99.5

<sup>a</sup> 79% of nitrogen and 1.0% of carbon monoxide.

<sup>b</sup> Tube 5.5 mm.

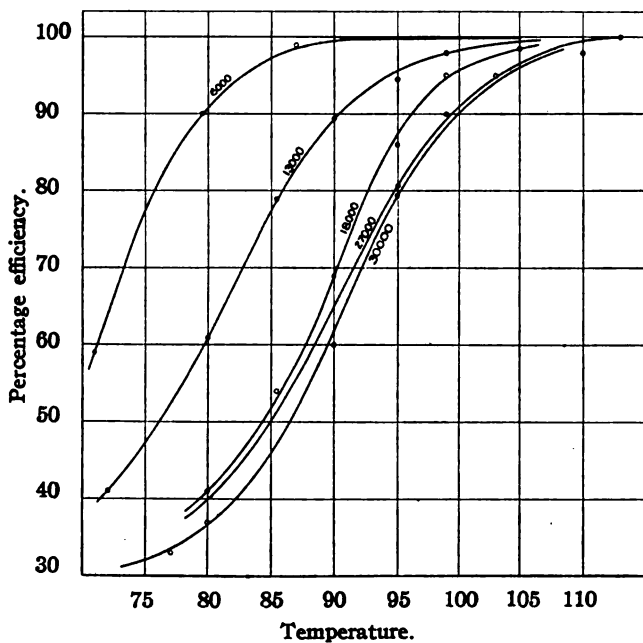


Fig. 3.

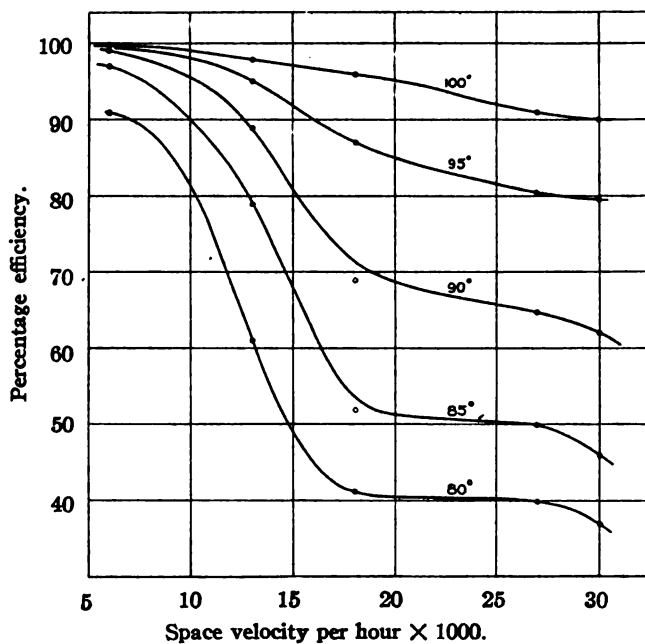


Fig. 4.

From these tables and figures it is evident that increasing the space velocity lessens the efficiency very greatly at 80° and relatively slightly at 99°; or, stated differently, to obtain high percentage efficiency at a high space velocity requires a relatively high temperature. If one sets 100° as the highest permissible temperature and 90% as the required efficiency, a space velocity as high as 27,000 can be attained.

**Concentration of Carbon Monoxide.**—Comparisons of the efficiency of combustion of 0.5 and 1.0% mixtures of carbon monoxide with air containing water vapor at 50 mm. mercury pressure were made under identical conditions, using copper tubes 5.5 mm. in diameter, with otherwise the same apparatus, the results of which are given in the following table.

TABLE V  
EFFICIENCY OF COMBUSTION WITH DIFFERENT CONCENTRATIONS OF CARBON MONOXIDE

Temperature ° C.	Space velocity per hour	Efficiency	
		For 0.5% of CO	For 1.0 % of CO
80	15,000	57	61
85	18,000	58	58
95	18,000	86	83

These results indicate that when adequate provision is made for the dissipation of the heat there is little, if any, gain in the percentage efficiency with different concentrations of carbon monoxide. An examination of Fig. 2 confirms this. There, in 7mm. tubes the heat dissipation was adequate at the lower temperatures and efficiencies, so that under these conditions the curves for 0.5% and 0.1% carbon monoxide are nearly identical; but at higher temperatures, where the efficiencies were much higher the heat evolution was greater, and the temperature therefore higher with 1% than with 0.5% carbon monoxide, and the two curves therefore diverge.

**Concentration of Oxygen.**—The combustion of one volume of carbon monoxide requires but half a volume of oxygen. In a technical utilization of this process it would be important to operate with as small an excess of oxygen as possible, as this excess must later be removed at the cost of an equivalent amount of hydrogen. A comparison of the results given in Tables II and III, where in the first case the concentration of the oxygen is 0.5% and in the second 20%, shows that the higher concentration has, at a space velocity of 6000, increased the efficiency by an amount roughly equivalent to a temperature rise of 15°. In practice, therefore, a balance would have to be struck between, on the one hand, the increased efficiency or correspondingly increased space velocity and, on the other, the cost of the extra hydrogen thus consumed.

**Carbon Dioxide.**—In the manufacture of hydrogen from water-gas the carbon dioxide is quite fully and easily removed by water-scrubbing,

and indeed the carbon dioxide thus removed may represent a useful by-product. Nevertheless, if this scrubbing could be omitted, or conducted in a less thorough and less expensive manner, an economy might be effected. It is of some interest, therefore, to study the effect of carbon dioxide on the efficiency of the catalytic oxidation. There is of course no possibility of a realization of the water-gas equilibrium at this temperature, but since, as pointed out above, carbon dioxide is very strongly adsorbed by Hopcalite, its introduction into the influent gases might be expected to effect a lowering of the efficiency. We have not tested this at all adequately, but using a dry gas mixture consisting of 0.5% of carbon monoxide, 20% of carbon dioxide, 10% of air, 60% of hydrogen and 9.5% of nitrogen at room temperature and a space velocity of 6000, there is no leakage of carbon monoxide when tested with the Hoolamite detector (0.03%).<sup>12</sup> This indicates that the effect of admixed carbon dioxide is slight.

**Hydrogen Sulfide.**—To test the effect of hydrogen sulfide, mixtures of 1% of carbon monoxide, 33% of carbon dioxide, and 64% of air with hydrogen sulfide were prepared by allowing the carbon dioxide to bubble through a concentrated solution of sodium sulfide. A strip of filter paper moistened with lead acetate placed in the effluent gases from the catalyst showed no change after several minutes, but immediately turned black when the gas mixture was by-passed around the Hopcalite. After 60 minutes' passage of this gas mixture the catalyst still oxidized the carbon monoxide completely at room temperature, and continued to do so for a half hour longer after the carbon dioxide, and hence the hydrogen sulfide, had been turned off. The next day, on further treatment with the same mixture containing hydrogen sulfide and carbon dioxide, the efficiency started at 100% but dropped after 45 minutes to 98%. Tested again on 1% carbon monoxide in air it gave a 99% efficiency which dropped after 2 hours to 95%. This indicates that the Hopcalite catalyst completely absorbs or destroys the hydrogen sulfide, and at first is not much impaired thereby, although continued exposure gradually destroys its activity. Examination of the catalyst at the end of the experiment confirmed this; the first 2 cc. of the Hopcalite had changed to a gray or black color. The hydrogen sulfide is presumably oxidized, and the resulting sulfur, or acids of sulfur, either react chemically with the Hopcalite, or form an adsorbed film which inhibits further action.

**The Temperature Rise in the Catalyst.**—The incandescence of the hydrogen, which invariably occurs when mixtures containing as much as 1% of carbon monoxide are catalytically oxidized by Hopcalite, is certainly a result of the too slow dissipation of the heat of combustion of the carbon monoxide. It is of, interest, therefore to inquire, first, what the maximum

<sup>12</sup> Ref. 2. Hoover, *J. Ind. Eng. Chem.*, 13, 770 (1921).

temperature rise could be for, say, a 1% carbon monoxide mixture; second, what general relation should obtain between the composition of the gas mixture, the space velocity, and the temperature rise; and third, to test this relation experimentally. For reasons of convenience these experiments were carried out not with the hydrogen-nitrogen mixture used in the Haber process, but with a carbon monoxide-air mixture. The maximum temperature rise and the temperature distribution are different in the two mixtures, but the same general principles should apply to both.

The maximum temperature rise will evidently occur when no heat is dissipated except to the effluent gas. An affluent gas mixture of the composition 1% of carbon monoxide, 20.7% of oxygen, and 78.3% of nitrogen, after combustion will have very nearly the composition 1%, 20.3%, and 78.7%, respectively. The average heat capacity of this mixture per hundredth of a mol of carbon monoxide at temperatures between room temperature and 100° is 6.87 mayers; the heat of combustion of this amount of carbon monoxide is 68,300/100 cal., and the maximum temperature rise will thus be 683/6.87 or 99.4° for a 1% mixture. No such rise, of course, takes place in our apparatus, so that the narrow copper tubes immersed in the well-stirred liquid bath must have dissipated a very large fraction of the heat evolved.

The general relation which should obtain between the composition of the gas mixture, the space velocity and the characteristic heat-dissipating capacity of the catalyst and its container can be deduced as follows. The heat supplied by the combustion of the carbon monoxide, when a steady state has been reached, must be equal to the sum of the heat lost to the gas and the heat dissipated by the catalyst container. Or, calling  $Q$  the heat of combustion per mol of carbon monoxide;  $C_1$  the heat capacity of the affluent gases per initial mol of carbon monoxide;  $S$  the space velocity;  $C_2$  the dissipation capacity of the gram molecular volume of the catalyst in mayers per hour;  $p$  the percentage by volume of carbon monoxide present; and  $\Delta t$  the temperature rise,

$$pQS = \Delta t(SC_1 + C_2)$$

and therefore

$$\Delta t = \frac{pQS}{SC_1 + C_2} = \frac{\frac{pQS}{C_1}}{S + C_2/C_1}.$$

Or, since  $Q = 68,300$  cal., and for small percentages of carbon monoxide  $C_1$  does not differ greatly from 6.87 mayers

$$\Delta t = \frac{99.4 pS}{S + C_2/6.87},$$

which is the desired relation. For adiabatic conditions, that is, when no heat is dissipated except to the effluent gas, this reduces to  $\Delta t = 99.4$



TABLE VI  
TEMPERATURE RISE IN CATALYST

Bore of reaction tube mm. CO, % Space velocity per hour, thousands Ratio of depths of layer	5.5						7						10					
	0.5			1.0			0.5			1.0			0.5			1.0		
	7.5	15	30	7.5	15	30	7.5	15	30	7.5	15	30	7.5	15	30	7.5	15	30
1/6.....	2.0	3.4	2.8	4.0	6.2	5.8	4.0	6.8	8.2	7.2	12.6	19.2	5.6	9.6	10.4	21.0		
2/6.....	1.0	2.8	4.0	1.6	4.6	7.6	3.0	6.8	10.0	4.4	12.0	22.4	3.1	8.8	5.2	14.2		
3/6.....	0.2	1.0	3.0	0.6	1.8	5.4	1.2	3.2	7.2	1.6	5.0	10.2	1.4	5.0	2.2	6.6		
4/6.....	0.2	0.6	1.6	0.4	0.8	2.8	0.2	1.2	2.2	0.4	1.4	2.8	0.8	3.0	1.0	3.6		
5/6.....	0.2	0.4	0.8	0.2	0.4	1.2	0.2	0.6	1.2	0.4	0.8	1.4	0.6	1.0	0.8	1.2		
Integrated Obs.....	0.72	1.50	2.10	1.40	2.60	3.94	1.66	3.19	4.94	2.68	5.78	9.78	2.22	4.89	5.34	8.59		
Average Calc.....	0.66	1.31	2.27	1.33	2.62	4.13	1.52	2.94	5.00	3.02	5.87	9.31	2.41	4.60	4.82	9.19		
C <sub>2</sub> /6.87 × 1/1000.....	506	479	608	521	554	581	215	217	240	288	241	242	159	137	131	157		
C <sub>1</sub> /C <sub>2</sub> Mean	550,000 ± 8%						237,000 ± 6%						146,000 ± 8%					

In all of these cases the efficiency was approximately 100% except in the measurements at a space velocity of 30,000, where the efficiency was approximately 90%.

$p$  as previously stated; that is, the temperature rise then amounts to 99.4° per cent. of carbon monoxide. For very rapid dissipation of heat this expression reduces to  $\Delta t = \frac{(99.4)(6.87)}{C_2} pS$ ; that is, the temperature

rise becomes very small, and proportional both to the percentage of carbon monoxide and to the space velocity.

To study this question experimentally we have measured the temperature rise in a Hopcalite catalyst, operating against mixtures containing 1% and 0.5% of carbon monoxide in air, at different space velocities, and in copper tubes of various diameters.

The purification, measuring and drying apparatus was identical with that already described. The catalyst container was a U-shaped copper tube with a side-tube soldered to a hole at the bottom of the U. Through this side-tube a glass tube carrying a copper-constantin thermocouple was inserted with its junction as nearly as possible at the center of the U. The catalyst was filled into both arms of the U, and different positions of the thermocouple with respect to the catalyst were obtained by altering in successive experiments the amount of the catalyst on either side of the thermocouple. In this way observations were made at  $\frac{1}{6}$ ,  $\frac{2}{6}$ ,  $\frac{3}{6}$ ,  $\frac{4}{6}$  and  $\frac{5}{6}$  of the distance from the inlet to the outlet surface of the catalyst bed. Three sizes of copper tubing, 5.5, 7.7 and 10 mm. in bore, were used; and the volume of catalyst was so adjusted that at corresponding space velocities, identical linear velocities were maintained. The catalyst tube was surrounded by an aqueous solution of calcium chloride kept accurately at 100°, and the affluent gases were preheated by passing through a coil of copper tubing immersed in the bath. The temperature rise in the tube during the oxidation of the carbon monoxide was measured by comparing the readings of the thermocouple while oxidation was taking place with those made when the moist air alone was passing through the catalyst. The results are collected in Table V. In every case the efficiency was 100% except in the measurements at 30,000 space velocity where it was approximately 90%.

To find how closely these results accord with the formula deduced above, it was first necessary to find an average value for the temperature rise ( $\Delta t$ ) in each tube. We have done this by plotting the five thermocouple readings for each tube at the same space velocity and with the same concentration of carbon monoxide, and integrating graphically the area under each curve. The resulting values are given after the heading "Integrated Averages Observed" in Table VI.

Inserting these values of  $\Delta t$  and the corresponding values of the percentage ( $p$ ) and the space velocity ( $S$ ), we have computed  $C_2/6.87$ . In those runs at 30,000 space velocity where the efficiency was only 90% we have made a proportionate allowance therefor. The resulting values are given in the bottom lines of Table V.  $C_2/6.87$  should be a constant for each diameter of tube, if the formula is correct. It can be seen that this is indeed the case, the average deviation of the individual values from the means being only 8%, or no more than corresponds to the experimental error. To show this more clearly we have calculated back to find what the average temperature rise should be from the average value of  $C_2/6.87$

for each tube. These values are given in the line headed "Integrated Averages Computed." The agreement is very close.

The average values of  $C_2/6.87$  for the tubes of different size would be expected to vary approximately inversely as the area of the tubes, or inversely as the squares of the bore. Actually the ratio of the  $C_1/C_2$  values is 1:1.6:3.8, while the inverse ratio of the squares of the bores is 1:1.6:3.3. Since the formula

$$\Delta t = \frac{99.4 pS}{S + C_2/6.87}$$

does indeed hold, and since under operating conditions it reduces practically to  $\Delta t = KpS$ , where  $K$  is a constant, it follows that for any permissible maximum value of  $\Delta t$  the product  $pS$  cannot exceed a certain limit, so that for a high percentage content of carbon monoxide only a small space velocity can be tolerated, and *vice versa*. This would indicate that a recirculation of the purified gas would be of no advantage, because for any decrease in  $p$  there would necessarily be an equivalent increase in  $S$ .

This formula does not, however, cover the whole situation.  $\Delta t$  is the *average* temperature rise, and this is not the most significant variable. The danger of combustion of the hydrogen is a function rather of the *maximum* rise in the catalyst mass, and this is by no means identical with or proportional to  $\Delta t$ . At low space velocities this maximum temperature rise always occurs at or very close to the front surface of the catalyst, but at high space velocities it is displaced toward the exit end of the tube.

To facilitate comparison, the maximum temperatures, ascertained by plotting the results in Table VI, are collected in Table VII.

TABLE VII  
MAXIMUM TEMPERATURE RISE IN DEGREES

Bore of tube, mm.....		5.5		7		10	
CO, %.....		0.5	1.0	0.5	1.0	0.5	1.0
Space velocity	7,500	2.4	4.8	4.2	7.4	5.8	10.6
	15,000	3.6	6.4	7.2	12.8	9.6	21.0
	30,000	4.4	8.6	11.0	24.8	..	..

It can be seen from Table VI that the maximum temperatures are quite closely proportional for the same tube and the same space velocity to the percentage of carbon monoxide. For the largest tube studied (10 mm.) they are also approximately proportional to the space velocity, but with the smallest tube the maximum temperature increases much more slowly than the space velocity, indeed approximately as the *square root* of the space velocity. It follows from this that, at least for small tubes, it would be advantageous to recirculate a fraction of the purified gas, mixing it with the raw gas. The physical interpretation of this effect, of course, is that by displacing the maximum temperature to the middle

of the catalyst a greater average temperature rise can be tolerated without danger of starting the oxidation of the hydrogen.

It can also be seen that the maximum temperature rise, like the average temperature rise, is approximately proportional to the square of the diameter of the tubes, and therefore approximately proportional to their area.

**Optimum Operating Conditions.**—On the basis of the above experimental results and discussion a number of postulates can be established relative to the optimum conditions for obtaining a complete, rapid, and economical preferential oxidation of the carbon monoxide, although many factors which are important in determining the optimum conditions for the technical operation of this process can only be ascertained from tests on full-size apparatus. On the one hand it is important to operate at as near the top of the temperature differential as possible, because the carbon monoxide is thereby rapidly and completely burned, or conversely very high space velocities can be utilized without a serious drop in efficiency. On the other hand, this temperature must be low enough to avoid any danger of combustion of the hydrogen at the higher temperature which will prevail within the catalyst, and of course to provide a margin of safety against accidental fluctuations in temperature. The "heat dissipating capacity" of the catalyst and its container should, of course, be as great as possible, this being secured by the use of small bore metallic tubes or a multicellular metallic container with its horizontal partitions made of wire gauze, the whole cooled by a circulating liquid. By a suitable design a disproportionate cooling could be applied to the region of maximum temperature rise, and thereby a uniform temperature maintained throughout the catalyst, or the maximum temperature displaced to a point at or near the exit surface of the catalyst. The simplest method of securing the latter arrangement is to adopt a two or multiple stage system, burning most of the carbon monoxide at a low temperature and relatively low efficiency (say 75%) in a first catalyst chamber, and then completing the combustion with the now much more dilute gas in a second chamber at a temperature not far from the top of the temperature differential. In this way a high space velocity coupled with a high efficiency could be attained safely. Several tests of this method were made, using 0.5 and 0.75% of carbon monoxide in mixtures consisting of 10% of air, 29.5% of nitrogen, and 60% of hydrogen, keeping the first catalyst tube at 82–87°, and the second at 90–99°, and a rapid and complete oxidation of the carbon monoxide was secured without difficulty.

In papers published since the completion of the above work Rideal and Taylor<sup>13</sup> and Rideal<sup>14</sup> have described catalysts consisting of specially activated copper oxide, as well as of iron oxide, with ceria and thoria as

<sup>13</sup> Rideal and Taylor, *Analyst*, **44**, 89 (1919).

<sup>14</sup> Rideal, *J. Chem. Soc.*, **115**, 993 (1919).

promoters, which preferentially oxidize carbon monoxide admixed with hydrogen at temperatures from  $100^{\circ}$  up to  $300^{\circ}$ . Data are given showing the relative amounts of carbon monoxide and of hydrogen oxidized in a 1:8 admixture with hydrogen at temperatures from  $160^{\circ}$  to  $400^{\circ}$ . The proportion of hydrogen oxidized increases very rapidly with rising temperature. Rideal calculates the relative amounts which should be oxidized on the basis of the Marcellin-Rice-Lewis radiation theory, and finds an approximate agreement, or at least a marked similarity in the shape of the experimental and theoretical curves at the higher temperatures.

At the lower temperatures, where only the copper oxide remains sufficiently active, the curves show a greater divergence, the copper oxide curve, extrapolated to  $100^{\circ}$ , indicating a ratio of hydrogen and carbon monoxide burned of about 0.15, while the theoretical equation gives a ratio of 0.004.

Applying this equation to our mixtures containing 0.5% of carbon monoxide and 89% of hydrogen, the ratio should be 0.0015 at  $100^{\circ}$ . Our experiments, in which any water which formed would have been collected and weighed, indicated no combustion of hydrogen greater than would correspond to this ratio, and do, therefore, afford some further confirmation of the equation.

### Summary

1. It has been shown that Hopcalite, which oxidizes carbon monoxide in air rapidly and catalytically at room temperatures, does not affect hydrogen in air under similar conditions, and that by its means carbon monoxide can be completely and continuously removed from a dry mixture containing, for instance, 0.5% of carbon monoxide, 89.5% of hydrogen, and 10% of air without any noticeable action on the hydrogen. A similar mixture containing 1% of carbon monoxide, on the other hand, liberates so much heat that under these conditions oxidation of the hydrogen sets in, and the catalyst is soon heated to incandescence and is destroyed.

2. It has been shown that moist mixtures of carbon monoxide and air, and of hydrogen and air require much higher temperatures for oxidation. In the presence of water vapor at a pressure of 50 mm. of mercury, carbon monoxide in a 0.5% mixture with air is completely oxidized at a temperature of  $90^{\circ}$  or lower. Hydrogen, on the other hand, mixed with air, does not begin to be oxidized under these conditions until a temperature of  $120$ – $125^{\circ}$  is reached. It is possible, therefore, to remove carbon monoxide completely and continuously from a mixture having, for instance, the composition 0.5% of carbon monoxide, 0.5% of oxygen, 24.75% of nitrogen, and 74.25% of hydrogen, and containing water vapor at a pressure of 50 mm. of mercury, without any considerable oxidation of the hydrogen. On the other hand, in a similar 1% carbon monoxide

mixture the hydrogen soon catches fire, and the catalyst becomes incandescent.

3. The effects on the efficiency of the catalyst of temperature, space velocity, carbon dioxide, hydrogen sulfide, and the concentration of the carbon monoxide have been studied.

4. Formulas for the temperature rise in the catalyst, the factor limiting the permissible concentration of the carbon monoxide, have been derived and have been experimentally verified at different space velocities, and in tubes of different diameters.

5. On the basis of these results, the proper conditions for the technical application of this method of removing carbon monoxide from hydrogen have been outlined.

6. Our results have been shown to be in agreement with the computations of Rideal, relative to the simultaneous oxidation of carbon monoxide and hydrogen.

7. A method for the analysis of small amounts of carbon monoxide in the presence of hydrogen has been worked out.

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[CONTRIBUTION FROM THE DEPARTMENT OF PHYSICAL CHEMISTRY, UNIVERSITY OF WISCONSIN]

## THE THERMAL DECOMPOSITION OF NITROGEN PENTOXIDE IN SOLUTION

BY ROGER H. LUECK

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The problem of reaction velocity is one of paramount interest to chemists. Attempts which have been made to explain the tremendous temperature coefficients of reaction velocities solely on the basis of the kinetic theory have not been verified by experimental data. For a 10° rise in temperature, reaction velocities are known to increase from 200 to 400%, whereas the number of collisions between the molecules increases by not more than 2%.

Arrhenius<sup>1</sup> early investigated the problem and found that the dependence of the velocity constant on the temperature could be satisfactorily expressed by the formula

$$\frac{d \ln k}{dT} = \frac{E}{RT^2} \quad (1)$$

where  $E$  is a quantity possessing the dimensions of energy, and which is found to vary but slightly with the temperature. Arrhenius sought an explanation of the huge temperature coefficients in postulating the existence of an equilibrium between "active" and "passive" molecules

<sup>1</sup> Arrhenius, *Z. physik. Chem.*, **4**, 226 (1889).

in which only those in the "active" form are in a condition to react. These "active" molecules are produced from the "passive" form by the absorption of a quantity of energy, corresponding to the  $E$  of the preceding equation, from their environment. The treatment of Arrhenius is unable to give any information concerning the internal processes involved in the absorption of this activating energy and, as Tolman<sup>2</sup> points out in a recent review, the physical significance of the quantity  $E$  is the subject of many conflicting opinions among investigators in this field.

Trautz,<sup>3</sup> Perrin<sup>4</sup> and Lewis<sup>5</sup> have attempted to correlate the value of  $E$  with the radiant energy available to a system undergoing chemical change. Their fundamental assumption is that  $E = Nh\nu$  where  $N$  is Avogadro's number,  $h$  the universal quantum constant, and  $\nu$  the frequency of the radiation which is absorbed by the reacting substance. The Arrhenius expression shows the natural logarithm of the reaction velocity to be a linear function of the reciprocal of the absolute temperature, and according to the Wien radiation law an exactly similar relation holds between the intensity of any monochromatic black-body radiation and the absolute temperature. From this very striking analogy Perrin has developed the following expression for the calculation of reaction velocity

$$k = se^{-\frac{Nh\nu}{RT}} \quad (2)$$

Here  $s$  is a constant having the dimensions of a frequency. This formula rendered in the logarithmic form leads to an equation exactly similar in form to that of Arrhenius.

References to the works of W. C. M. Lewis, Dushman and Tolman who have studied the question and arrived at similar expressions may be found in the excellent review of the last named.

Any problem of this nature offers a wide field of opportunity to the theoretical chemist and quite naturally the major portion of the literature on the subject is of a theoretical character. The amount of experimental data for checking up the various theories is at present unduly limited.

Cox<sup>6</sup> has recently published a paper in which the problem is attacked experimentally. It follows from the Perrin-Lewis radiation hypothesis that any reaction medium which increases the velocity of a given reaction, *i. e.*, by increasing the density of the particular radiation frequency which is absorbed by the reacting molecules, should decrease the temperature

<sup>2</sup> Tolman, *THIS JOURNAL*, **43**, 269 (1921).

<sup>3</sup> Trautz; for summary of earlier papers see *Z. anorg. allgem. Chem.*, **102**, 81 (1918) and **106**, 149 (1919).

<sup>4</sup> Perrin, *Ann. phys.*, **11**, 5 (1919).

<sup>5</sup> W. C. M. Lewis. See particularly *J. Chem. Soc.*, **111**, 389, 457, 1086 (1917); **113**, 471 (1918); *Phil. Mag.*, **39**, 26 (1920); *THIS JOURNAL*, **43**, 1288 (1921).

<sup>6</sup> Cox, *J. Chem. Soc.*, **119**, 142 (1921).

coefficient of the reaction velocity. With this in mind, Cox has studied the reaction of bromo-acetophenone with aniline in a number of organic solvents and also the reaction between sodium  $\beta$ -naphtho-oxide and ethyl iodide in some of the liquid alcohols. His results in general do not corroborate the theories of Perrin and Lewis. It should, however, be observed that a number of disturbing influences enter into these reactions which might readily explain the observed discrepancies. Since both reactions are of the second order there are the varied complications arising from molecular collision, viscosity of the solvent, the absorption of radiant energy by more than one species of molecule, and, in addition, in the second named reaction the ionization of the sodium  $\beta$ -naphtho-oxide. It should be mentioned that Cox himself has pointed out some of these possibilities.

Since any true monomolecular reaction does not depend upon molecular collision, information concerning the velocity constant should throw light on the mechanism of this absorption of radiant energy, provided however, that some of the other factors which may have influenced the work of Cox are likewise absent. The ideal system for this study is a monomolecular reaction, uncatalyzed by the walls of the containing vessel, taking place in solvents where there is little likelihood of any loose solvent-solute complexes or of any ionization of the solute. The reaction in solution possesses an advantage over a gas phase reaction in that it offers a wider variation of conditions under which the reaction may take place, *e. g.*, the concentration of reacting substance, and also enhances the opportunities for varying the reaction medium.

Daniels and Johnston<sup>7</sup> have studied the decomposition of nitrogen pentoxide in the gas phase and have found it to follow the course of a true monomolecular reaction and to be entirely uncatalyzed by the vessel walls of glass. The present paper presents the results of some experiments in which this same reaction has been studied in solution and its velocity followed by measuring the volume of oxygen evolved. It is preliminary to a research being conducted by Dr. Farrington Daniels of this laboratory in an attempt to uncover some definite relationship between the reaction velocity and the absorption of radiation within the solution.

### Preparation and Purification of Materials

The nitrogen pentoxide was prepared as described by Daniels and Bright<sup>8</sup> in their study of the vapor pressure of the substance.

Uncombined water was removed from nitric acid by two distillations from conc. sulfuric acid and this 100% product was dehydrated with phosphorus pentoxide. The nitrogen pentoxide thus formed was distilled from the phosphoric acid, through phosphorus pentoxide, and condensed in a U-tube surrounded by a freezing mixture, at  $-20^{\circ}$ . A second distillation through phosphorus pentoxide in a current of ozonized air sufficed

<sup>7</sup> Daniels and Johnston, *THIS JOURNAL*, **42**, 1131 (1920).

<sup>8</sup> Daniels and Bright, *ibid.*, **43**, 53 (1921).



to produce snow-white, anhydrous crystals of nitrogen pentoxide. The ozone prevents the formation of nitrogen peroxide. Immediately before use the product was again distilled through phosphorus pentoxide into a second, smaller U-tube which was then sealed off and the material thus preserved on ice until required.

Sulfur was removed from the carbon tetrachloride used as a solvent by allowing to stand over mercury for a week with frequent shaking. After drying with phosphorus pentoxide the liquid was fractionated through a 5-bulb column. Only the middle portion, distilling off over a range of  $0.03^\circ$ , was used in the experiments. The final product gave no test for chloride ion.

The chloroform was purified by shaking thrice with a solution of sodium carbonate to remove alcohol and traces of hydrochloric acid. After washing thoroughly with distilled water the material was dried over calcium chloride and distilled from phosphorus pentoxide through a fractionation column. The final product gave no test for moisture, alcohol or chloride ion.

The solution of the nitrogen pentoxide in the solvents was effected in such a way as to prevent the access of atmospheric moisture. Placed in a desiccator immersed in a freezing mixture these solutions could be kept for several days without any marked deterioration.

### Experimental

**Apparatus.**—The velocity of the decomposition was determined by the gasometric method in the apparatus shown in Fig. 1, the whole being set up in duplicate. Reaction

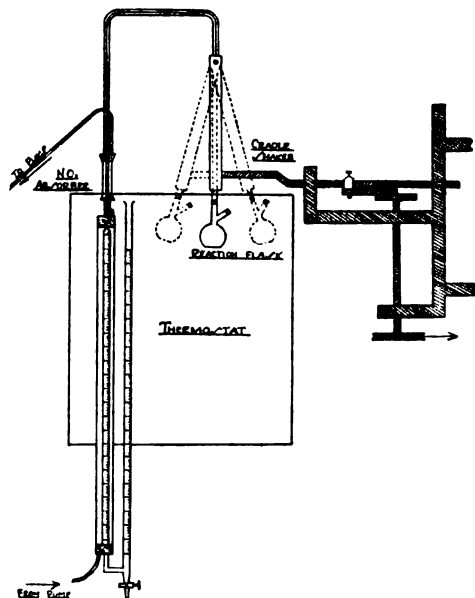


Fig. 1.

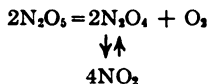
flasks, similar to those used by Walton<sup>9</sup> and his students in their hydrogen peroxide studies, were supported by a shaking cradle in a thermostat maintained constant to  $\pm 0.015^\circ$  and connected by means of capillary tubing to the tops of jacketed 100cc.

<sup>9</sup> Walton, *Z. physik. Chem.*, **47**, 185 (1904).

burets in which the oxygen evolved was collected. Thorough shaking was insured by the addition of glass beads to the reaction flasks. The outside of the flasks was painted with several coats of black shellac to exclude light.

The greatest difficulty was experienced with the indispensable rubber connection between the reaction flasks and the capillary tubing which carried the oxygen over into the burets. The action of the oxides of nitrogen on rubber is very vigorous. Of all forms, pressure tubing functioned the worst. The problem was ultimately solved by inserting one length of red rubber tubing inside another just large enough to take it with a very thin layer of vaseline between the two. A 20cm. length of capillary tubing was fused to the reaction flasks so that the rubber connection was made at some distance from the flasks and at the axis of rotation of the shaking cradle.

The reaction was assumed to take place the same as in the gas phase in accordance with the following equation



Most of the nitrogen dioxide formed remained dissolved in the solvent. However, some always passed into the gaseous state and tended to pass over into the burets, rendering the readings erroneous. To prevent this, 15 cm. of 12mm. glass tubing, filled with glass wool wet with conc. sulfuric acid and water-jacketed, was interposed between the burets and the reaction flasks. The free space above the solution in the flasks was always maintained as small as possible in order to render negligible the errors introduced by the passage of some nitrogen dioxide into the gas phase.

It was essential to know whether the actual decomposition was occurring in solution as desired or in the free space above the solution. The following considerations proved the invalidity of the latter possibility. The total amount of nitrogen pentoxide present in the system, as measured by the total volume of oxygen evolved, would have to be initially present in the free space if the velocity constants were to remain regular. Such a condition would necessitate an initial pressure of several atmospheres in almost every case, whereas the experiments were all carried out under atmospheric pressure. A second proof was obtained by direct experiment. When the shaking device was at rest no increase in volume was registered in the burets, provided the rest period was not excessively long. If, after such a stationary period, the shaking was commenced, oxygen was rapidly evolved, equilibrium attained within a minute, and the volume of oxygen thus obtained with intermittent shaking was exactly equal to that which would have been evolved with continuous shaking over an equal interval of time under the same conditions. This is conclusive proof that the decomposition occurs entirely in the solution, the oxygen which is formed when the shaker is not in action being retained in the solvent as a supersaturated solution.

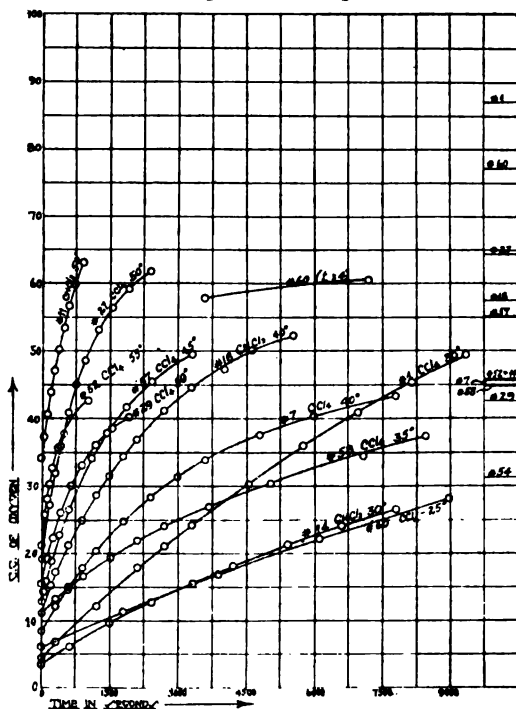
The evolved gas was collected in gas burets and measured over the liquid which was being used as a solvent in the reaction flasks. A leveling tube connected with the bottom of the burets made possible the rapid adjustment of liquid levels. Water at constant temperature was forced through the buret jackets, thus obviating a variable temperature correction.

**Method.**—All connections between the burets and the reaction flasks rendered gas-tight, a measured volume of the solution to be investigated was pipetted into the reaction flasks which had previously been thoroughly cleaned and dried. The flasks were stoppered with the accurately fitting glass stoppers, the shaking cradle lowered and set in motion. After waiting until 15–20 cc. of gas had been evolved, in order to allow for thermal

lag and the disruption of an initial condition of supersaturation of oxygen in the solvent, volume readings were taken at measured intervals. All readings were corrected to 0° and 760 mm. pressure in order that the velocity constants obtained would be independent of the barometric pressure. Time readings were taken on a stop-watch. The final observation, which was a measure of the quantity of nitrogen pentoxide initially present, was made when no further increase in volume was noticed after a long period of time.

Experiments were not carried out above 55°, for in so doing accuracy would be sacrificed for speed in observation and the reaction would be well-nigh complete before the shaking had effected a regular evolution of gas. Likewise, nothing was done below 25° because of the long time involved in the completion of an experiment at lower temperatures.

Calculations.—Fig. 2 represents a graphical grouping of the results obtained where the volume of oxygen evolved is plotted against time. Duplicates are not shown. Graphical interpolation over equal intervals of



of the reaction only the total volume of gas evolved and the differences between successive readings are necessary.

TABLE I  
Carbon Tetrachloride. 40°  
 $V_0 = 10.75$  cc.  $V_\infty = 45.50$  cc.

$t$ Sec.	$V_t - V_0$ Cc.	$V_\infty - V_t$ Cc.	$K \times 10^{-4}$
0	0.00	34.75	..
300	3.42	31.33	..
600	6.30	28.45	3.21
900	8.95	25.80	3.26
1200	11.40	23.35	3.32
1500	13.55	21.25	3.14
1800	15.52	19.23	3.33
2100	17.30	17.45	3.24
2400	18.90	15.85	3.20
2700	20.35	14.40	3.20
3000	21.70	13.05	3.28
3600	23.95	10.80	3.15
4200	25.65	9.10	..
4800	27.25	7.50	3.22
6000	29.55	5.20	3.05
$\infty$	34.75	0.00	..
			Av. 3.22
			Duplicate Av. 3.22
			Mean 3.22

Table I presents a typical calculation of the velocity constants from the data. The column headed  $V_\infty - V_t$  gives the difference between the final volume  $V_\infty$  and the volume at any time  $V_t$ . The reaction-velocity constants shown in the last column were calculated directly from the data in the first and third columns with the aid of the familiar formula

$$k = \frac{2.302}{t_2 - t_1} \log \frac{V_\infty - V_{t_1}}{V_\infty - V_{t_2}}$$

The values of  $t_2$  and  $t_1$ , chosen for the calculations, are successive times shown in the first column; all times are expressed in seconds.

TABLE II  
VALUES OF THE VELOCITY CONSTANT ( $k \times 10^{-4}$ )

Temperature °C.	Carbon tetrachloride			Chloroform		
	1	2	Mean	1	2	Mean
55	21.1	21.3	21.2			
50	11.5	11.7	11.6	12.7	12.6	12.8
					13.0	
45	6.37	5.95	6.11			
	6.13	5.97				
40	3.22	3.22	3.22	3.74	3.89	3.81
35	1.62	1.62	1.62			
30	0.841	0.842	0.8415	1.03	1.02	1.025
25	0.421	0.398	0.409			

In order to conserve space the other results have not been tabulated in this form but are shown condensed in Table II.

### Results

The matter of the temperature coefficient of the reaction velocity is of considerable interest. It has been previously mentioned that those agencies which increase the reaction velocity decrease the temperature coefficients. Skrabal<sup>10</sup> has arrived at the very general conclusion that the "relations between reaction velocity, temperature effects, influence of solvent, added catalyst and photochemical action are all essentially the same; accordingly, change in the reaction velocity effected by any one of these factors diminishes as the magnitude of the velocity constant increases." Table III shows how well the data obtained in this investigation agree with this deduction from the theories of Perrin and Lewis. It will be observed that the temperature coefficients in the case of chloroform, in which the reaction proceeds more rapidly than in carbon tetrachloride, are smaller than those in carbon tetrachloride for corresponding temperature intervals. Similarly with increasing temperature the values of the temperature coefficients show a uniform decrease.

TABLE III  
TEMPERATURE COEFFICIENTS OF THE REACTION VELOCITY

Temp. interval ° C.	Carbon tetrachloride	Chloroform
------------------------	----------------------	------------

55/45	3.47	..
45/35	3.77	..
35/25	3.96	..
50/40	3.60	3.33
40/30	3.83	3.73

Dushman<sup>11</sup> has proposed a formula for monomolecular reactions by which the magnitude of the velocity constant at any temperature may be calculated from its value at one particular temperature. He assumes with Perrin and Lewis that  $E = Nh\nu$  but does not specify any mechanism for the interaction of radiant energy. His equation is of the same form as that of Arrhenius and Perrin (see Equations 1 and 2) but Dushman ingeniously postulates that the unknown quantity  $s$ , which has the dimensions of a frequency, is the same frequency already introduced in the expression  $E = Nh\nu$ . This leads him to the equation

$$k = \frac{E}{Nh} e^{-\frac{Nh\nu}{RT}} \quad (3)$$

which for purposes of calculation may be written

$$\log k = 10.0203 + \log E - (E/4.571 T) \quad (4)$$

<sup>10</sup> Skrabal, *Monatsh.*, **37**, 495 (1916).

<sup>11</sup> Dushman, *THIS JOURNAL*, **43**, 397 (1921).

Dushman has tested this equation with the experimental data obtained by Trautz and Bhandarkar<sup>12</sup> for the monomolecular decomposition of phosphine above 920° K. and finds excellent agreement within the limit of experimental error.

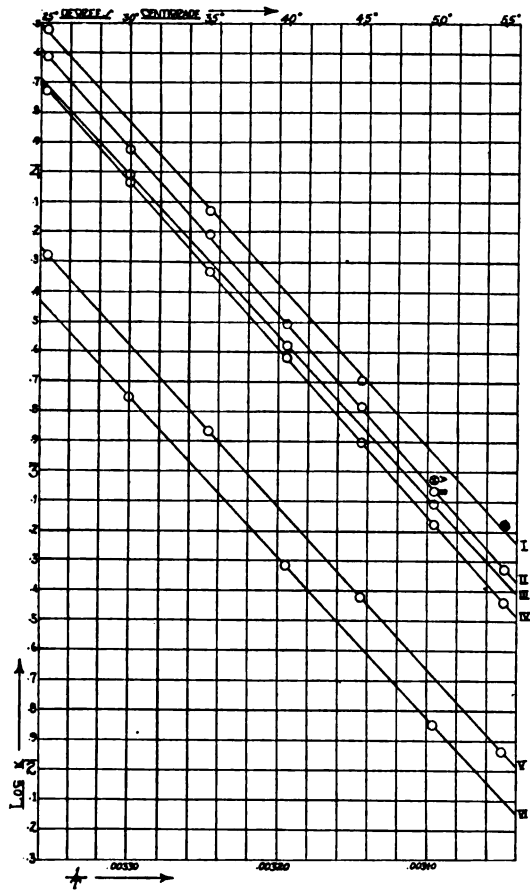


Fig. 3.—I. Gas phase; II. Carbon tetrachloride; III. Chloroform; IV. Carbon tetrachloride (calculated); V. Gas phase (calculated); VI. Chloroform (calculated).

Tolman<sup>2</sup> has applied this equation to the results obtained by Daniels and Johnston<sup>7</sup> for the decomposition of nitrogen pentoxide in the gas phase and finds a far better agreement with the experimental data than can be obtained using the older expressions developed by Trautz and by Lewis. Table IV and Fig. 3 show a comparison of the results obtained in this investigation with those calculated by means of Dushman's equation.

<sup>12</sup> Trautz and Bhandarkar, *Z. anorg. allgem. Chem.*, 106, 95 (1919).

By integrating the expression of Arrhenius and converting to common logarithms we obtain

$$E = \frac{1.98 T_2 \times T_1 \times 2.302 \log k_2/k_1}{T_2 - T_1} \quad (5)$$

By substituting the values of the reaction velocity constants,  $k_2$  and  $k_1$ , corresponding to two different absolute temperatures,  $T_2$  and  $T_1$ , the values of  $E$  were calculated.

TABLE IV  
Carbon Tetrachloride

Temp. ° C.	$1/T \times 10^{-3}$	$K$ (obs.)	$\text{Log } k$ (obs.)	$E$ cal.	$\text{Log } k$ (calc.)	$K$ (calc.)
55	0.30488	$21.2 \times 10^{-4}$	$\bar{3}.32634$	25,292	$\bar{3}.438$	$27.4 \times 10^{-4}$
50	0.30960	11.6	$\bar{3}.06446$		$\bar{3}.175$	15.0
45	0.31446	6.11	$\bar{4}.78604$	26,070	$\bar{4}.904$	8.02
40	0.31949	3.22	$\bar{4}.50786$	25,242	$\bar{4}.624$	4.21
35	0.32468	1.62	$\bar{4}.20952$	26,218	$\bar{4}.335$	2.16
30	0.33004	0.841	$\bar{5}.92480$	24,222	$\bar{4}.036$	1.09
25	0.33557	0.409	$\bar{5}.61172$	25,770	$\bar{5}.728$	0.535

Av. 25,469

Chloroform

50	0.30960	12.8	$\bar{3}.10721$	24,252	$\bar{3}.848$	70.6
40	0.31949	3.81	$\bar{4}.58092$		$\bar{3}.318$	20.8
35	0.33004	1.02	$\bar{4}.01072$	24,648	$\bar{4}.754$	5.68

Av. 24,450

### Theoretical

In Fig. 3 these same results are graphically expressed. It will be observed that in every case the line representing the results calculated by the Dushman equation for any particular solvent lies exactly parallel to that representing those experimentally determined and plotted according to the Arrhenius expression. It is apparent, however, that no physical significance can be attached to this fact since both expressions are equations for a straight line and their slopes are made numerically equal by setting  $E$  equal to  $Nh\nu$ , as Dushman has done in his derivation.

It is of importance to note that the differences between observed and calculated values for the gas phase and for chloroform are exactly equal while those for carbon tetrachloride are considerably less. The full significance of this fact is at present not quite clear, but if fully understood it might be of assistance in explaining the mechanism of a monomolecular

reaction. The magnitude of these differences as compared with those obtained when  $k$  is calculated from the equations of Trautz and Lewis, as Tolman has done shows quite conclusively that the work of Dushman is a step in the right direction, but likewise indicates the necessity for the introduction of some *variable* factor into the equation which will account for the variable differences obtained with different reaction mediums. Undoubtedly the form of the equation is correct since it is the same as that of Arrhenius which does give quite satisfactorily the dependence of the velocity constant on the temperature. Likewise the values of  $N$  and  $h$  are constant and have been checked by a variety of methods. This leaves but the one alternative: that the expression,  $\nu = E/Nh$ , is not entirely applicable in this connection. The value of  $\nu$  as calculated from the data obtained in the gas phase reaction is  $1.16 \mu$ , when expressed as a wavelength, for carbon tetrachloride  $1.13 \mu$  and for chloroform  $1.18 \mu$ . In their study of the photochemical decomposition of nitrogen pentoxide, Daniels and Johnston have shown that light of this wavelength is not effective in bringing about decomposition, and further that nitrogen pentoxide possesses no absorption bands in this region. From similar considerations Langmuir<sup>13</sup> has suggested that the whole radiation theory for chemical action be abandoned.

The present writer feels that there lies considerable promise in the suggestion of Tolman<sup>14</sup> who holds that  $E$  is in general not a constant nor does it correspond to a single frequency except in the limiting case, adopted by Perrin, where only a spectrum "line" is active. He replaces the constant,  $\nu$  or  $E/Nh$ , of the Dushman equation with a variable,  $e^{\int \frac{d\nu}{RT}}$ , thus taking into account the fact that photochemical reactions are often brought about by radiant energy having a wide range of frequencies and also the probability that the molecules, having themselves different internal states, may require different quantities of energy for activation. This range of activating frequencies must be specific for any one substance but the particular frequency within the band which is most active can readily be thought of as varying with different reaction mediums. The introduction of a variable into the Dushman equation should account for the variable differences obtained in the calculation of the velocity constants for the decomposition of nitrogen pentoxide, using the expression as it stands at present.

*The catalytic effect of nitrogen pentoxide.*—It was found in the photochemical work of Daniels and Johnston that blue light of wavelength between 400 and 460  $\mu\mu$  was effective in decomposing the pentoxide but *only* in the presence of brown nitrogen dioxide which shows almost complete absorption of light in this region. Their other work carried out in

<sup>13</sup> Langmuir, *THIS JOURNAL*, 42, 2190 (1920).

<sup>14</sup> Tolman, *ibid.*, 42, 2506 (1920).



the absence of light indicated that the nitrogen dioxide was not an auto-catalyst to the dark reaction.

In this connection the two points, A and B of Fig. 3, obtained at 50° in carbon tetrachloride solution are important. Point A was obtained using a solution of the nitrogen pentoxide where special precautions were observed to keep the initial concentration of nitrogen dioxide as low as possible, whereas Point B represents the velocity constant in a solution previously saturated with the dioxide. It should be stated that, despite the precautions observed in the former case, the initial concentration of nitrogen dioxide was considerably greater than that which existed initially in any of the experiments carried out in the gas phase.

Comparing this odd value, A, with those obtained in the gas phase and with the others obtained in carbon tetrachloride solution, one is led to believe that nitrogen dioxide is an auto-catalyst to the dark reaction and that the catalytic effect is proportional to the amount present up to a "limiting concentration" which is rather low. At this point further increase in the nitrogen dioxide present has little effect on the velocity constant.

The fact that the values obtained for the velocity constant in carbon tetrachloride lie so well on the straight line, Fig. 3, despite the fact that no attempt was made to maintain a constant initial value for the nitrogen dioxide concentration, receives a ready explanation from the above considerations, for, in all cases except that represented by Point A, the initial concentration was considerable and above that designated as the "limiting concentration." Similarly, in the gas phase, where this initial concentration of nitrogen dioxide was always very low and in the region where slight variation in its content has an appreciable effect on the rate of reaction, one would naturally expect to find lower values for the velocity constants in general and greater variations from the straight line when plotted as in Fig. 3. Results, indicative of this same phenomenon, were obtained by Daniels and Johnston in their study of the photochemical decomposition of nitrogen pentoxide.

Further experiments will be carried out to determine what effect the nitrogen dioxide and the nitrogen tetra-oxide, with which it must exist in equilibrium, have on the absorption spectra of the solutions in which the velocity of this reaction is measured.

The writer wishes to express his sincerest thanks to Dr. Farrington Daniels at whose suggestion and under whose direction this work was done.

### Summary

1. The velocity of the decomposition of nitrogen pentoxide in carbon tetrachloride and in chloroform solutions has been determined gasometrically between 25° and 55°. Such systems are of special value in study-

ing the new theories concerning the relation of radiant energy to chemical action.

2. The fact that the velocity constants obtained in solution so closely approximate those obtained in the gas phase by Daniels and Johnston is of peculiar significance since, as far as the writer is aware, this is the first time that the velocity of a monomolecular reaction has been measured under so wide a variation of conditions.

3. The experimental facts show the energy of activation or the critical increment to be practically independent of the temperature.

4. It has been shown that, in accordance with a necessary deduction from the Perrin-Lewis radiation theory, a change in reaction velocity brought about by temperature effects or the influence of solvent diminishes as the magnitude of the velocity constant increases.

5. A comparison has been made between the values of the velocity constant experimentally obtained and those calculated from the critical increment,  $E$ , by means of the equation recently proposed by Dushman. Although the agreement is not exact, it is far better than can be obtained using the older equations developed by Trautz and Lewis.

6. The nitrogen peroxide formed in the reaction has been shown to exert an auto-catalytic effect on the thermal decomposition of the nitrogen pentoxide.

7. This work is at present being extended in this laboratory to other solvents and to a study of the absorption spectrum of nitrogen peroxide in the various solvents.

MADISON, WISCONSIN

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[CONTRIBUTION FROM THE LABORATORY OF PHYSICAL CHEMISTRY, PRINCETON UNIVERSITY]

## THE SIZES OF ATOMS IN CRYSTALS

By ROBERT N. PEASE<sup>1</sup>

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The author has recently shown<sup>2</sup> that molecular volumes, as revealed by the constant  $b$  of van der Waals' equation, are consistent with the view that the volumes of atoms and groups of atoms depend upon the number and arrangements of electrons about the positive nuclei of the atoms rather than on the particular kinds of atoms involved. It was shown, for example, that the volumes of the nuclear carbon, nitrogen and oxygen atoms in methane, ammonia and water respectively, are nearly the same and equal to that of the rare gas, neon. The number and arrangements of electrons about the positive nuclei of these nuclear atoms and of neon are the same for all. Similarly, the volumes of the

<sup>1</sup> National Research Fellow in Chemistry.

<sup>2</sup> Pease, *THIS JOURNAL*, 43, 991 (1921).

oxygen molecule and the carbon atoms in ethylene were shown to be the same. In the present paper, it is proposed to apply this point of view to an examination of the interatomic distances<sup>3</sup> in crystals of the diamond type.

It is now known that diamond,<sup>4</sup> silicon,<sup>5</sup> gray tin,<sup>6</sup> carborundum,<sup>7</sup> zinc sulfide,<sup>4</sup> the cuprous halides,<sup>8</sup> and silver iodide,<sup>9</sup> all crystallize in the so-called diamond-type lattice. Neutral carbon, silicon and tin atoms all require 4 electrons to complete their outer shells. It is evident that in the diamond type of lattice the atoms can all acquire these by sharing pairs of electrons with the 4 surrounding atoms. It is obvious that in the case of carborundum (SiC) the same is true, for a crystal of this substance differs from one of the diamond or silicon only in that half of the atomic kernels are replaced by those of the other element.

For the salts which crystallize in the diamond lattice relations of a similar sort hold. Let it be assumed that in zinc sulfide each zinc atom has lost 2 electrons to a sulfur atom, thereby completing the latter's octet. The zinc atom will then require 8 additional electrons in its outer shell (corresponding to krypton) to complete the latter. Evidently, if it shares with each of the 4 surrounding sulfide ions a pair of electrons belonging to the latter, it can acquire the 8 it needs. There thus appears to be a very definite chemical reason for zinc sulfide crystallizing in the diamond type of lattice. In the cuprous halides and silver iodide the same relations hold. The metal atom may be regarded as giving up 1 electron to the halogen atom, thereby completing the latter's octet and then obtaining the 8 electrons which it requires to fill out its outer shell by sharing electrons with the 4 halide ions surrounding it.

Of the kinds of atoms contained in these substances which crystallize in the diamond lattice, carbon is of the neon type; silicon, sulfur and chlorine are of the argon type; copper, zinc and bromine, of the krypton type; and silver, tin and iodine, of the xenon type. It might be surmised from the conclusions reached in the earlier paper that with a single value for the radius of each of these characteristic types, the inter-atomic distances for all these substances could be derived. This is in fact the case. For the neon type, the value for the radius of the carbon atom in diamond,

<sup>3</sup> This term applies, of course, to the distances between the *centers* of the atoms. This is expressed in Ångstrom units. ( $1 \text{ Å. U.} = 10^{-8} \text{ cm.}$ ).

<sup>4</sup> W. H. and W. L. Bragg, "X-Rays and Crystal Structure." G. Bell and Sons, 1918.

<sup>5</sup> Debye and Scherrer, *Physik. Z.*, 17, 277 (1916).

<sup>6</sup> Bijl and Kolkmeijer, *Verslag Akad. Wetenschappen Amsterdam*, 27, 359 (1918).

<sup>7</sup> Burdick and Owen, *THIS JOURNAL*, 40, 1749 (1918). See also Hull, *Phys. Rev.*, [2] 13, 292 (1919).

<sup>8</sup> Wyckoff and Posnjak, *THIS JOURNAL*, 44, 30 (1922).

<sup>9</sup> Wilsey, *Phil. Mag.*, 42, 262 (1921).

*i. e.*, one-half the distance between nearest atomic centers, 0.77 Å. U., is taken. For the argon type, the value for silicon is taken. Debye and Scherrer give this as  $\frac{2.35}{2} = 1.18$  Å. U. According to Gmelin-Kraut's Handbuch,<sup>10</sup> however, numerous determinations place the density of silicon at 2.49, which gives  $\frac{2.30}{2} = 1.15$  Å. U., for the radius of the silicon atom. This is the value used in the calculations. For the krypton type there is available the value for the distance between centers in cuprous bromide, 2.52 Å. U. One half this, 1.26 Å. U., is taken as the value for the radius of atoms of the krypton type. For the xenon type, the value for gray tin,  $\frac{2.80}{2} = 1.40$  Å. U., has been chosen.

Using these four constants, the interatomic distances for the 9 substances have been calculated with the following results.

TABLE I  
INTER-ATOMIC DISTANCES

Type		Radius		Distance between nearest centers				
		Å. U.		Calc.	Observed	Diff.	From Bragg's radii	Diff.
Neon	(C)	0.77	Diamond	1.54*	1.54	....	1.54	....
Argon	(Si,S,Cl)	1.15	Silicon	2.30*	2.30	....	2.35	....
Krypton	(Cu,Zn,Br)	1.26	Gray tin	2.80*	2.80	....	2.80	....
Xenon	(Ag,Sn,I)	1.40	SiC	1.92	1.90	+0.02	1.95	+0.05
			ZnS	2.41	2.35	+0.06	2.35	0
			CuCl	2.41	2.38	+0.03	2.43	+0.05
			CuBr	2.52*	2.52	....	2.57	+0.05
			CuI	2.66	2.63	+0.03	2.78	+0.15
			AgI	2.80	2.83	-0.03	3.18	+0.35

\* These values taken as standards.

The agreement is evidently very good. Substances which according to the hypothesis should be the same are gray tin and silver iodide, the values for which are 2.80 and 2.83 Å. U., respectively, and zinc sulfide and cuprous chloride, the values for which are 2.35 and 2.38 Å. U., respectively. Since the ions of zinc sulfide are doubly charged while those of cuprous chloride are singly charged, one might expect that the interatomic distance would be less in the former. The relatively slight difference between the two (0.03 Å. U.) as compared with that between an alkaline earth sulfide and the corresponding alkali chloride (*e. g.*,  $d_{\text{KCl}} - d_{\text{CaS}} = 0.36$  Å. U.) is good evidence for the close-packed nature of the diamond lattices in which zinc sulfide and cuprous chloride crystallize.

Zinc oxide, though not crystallizing in the diamond lattice, nevertheless has the same relative arrangement of atoms.<sup>11</sup> The inter-atomic distance is 1.97 Å. U. The calculated value would be  $0.77 + 1.25 = 2.02$  Å. U.

<sup>10</sup> Gmelin-Kraut, "Handbuch der anorganischen Chemie," Carl Winter, 1912, 3, 1, 110.

<sup>11</sup> W. L. Bragg, *Phil. Mag.*, [6] 39, 647 (1920).

It is of interest to note that crystals of silver iodide and of gray tin are isosteric, as Langmuir defines the term, in that they differ only in the distribution of net charge among the positive nuclei, the charge on each tin nucleus being 50 units while the charges on the silver and iodine nuclei are 47 and 53 units respectively. The number and arrangement of electrons are the same in both. Zinc sulfide and cuprous chloride crystals are also isosteric.

The manner of regarding inter-atomic distances as depending on the rare gas type of atom involved and on the type of lattice, as exemplified in the above analysis, is suggested as an alternative to W. L. Bragg's method of treating these values.<sup>12</sup> Bragg considers that the atoms in a crystal can in all cases be regarded as close-packed spheres and that it is possible "to assign to the sphere representing an atom of any element a constant diameter characteristic of that element." As Bragg has pointed out, the resulting atomic radii are not wholly consistent with the present day ideas concerning atoms. He is constrained to assume, for example, that the radius of the sodium ion is 1.78 Å. U. while that of the fluoride ion, which has the same rare-gas (neon) structure, is only 0.68 Å. U., less than half as large. The radius of the iodide ion even, which is of the xenon type, is according to Bragg only 1.40 Å. U. Now one would expect on the basis of the Lewis-Langmuir theory that the outer shells of the sodium and fluoride ions are the same size and that of the iodide ion is much larger. In the alkali halides, however, the completed outer shells of the ions are probably considerably separated due to the presence of repulsive as well as attractive forces within the lattice. Evidently, Bragg's values for the atomic radii arbitrarily place responsibility for this free space separating the ions more largely upon the sodium ions, but on other metal ions as well. These, therefore, have abnormally large values. The reason why the values assigned to the negative ions are so small is that the same value must serve for cases in which the atoms of the negative elements are sharing electrons and are therefore very much closer together, there being no free space separating them.

As evidence that the assumption of constant atomic radius can be only approximately correct, the following may be cited. The distance between carbon atoms in diamond is 1.54 Å. U. In graphite, it is 1.45 Å. U.,<sup>13</sup> a discrepancy of 0.09 Å. U. or 6%. Again, in both metallic calcium and calcium oxide, the calcium atoms are arranged on a face-centered cubic lattice. The distance between nearest calcium atoms in the metal is 3.93 Å. U.<sup>14</sup> The distance between the corresponding calcium atoms in the oxide, if these have a constant diameter might be expected to be

<sup>12</sup> W. L. Bragg, *Phil. Mag.*, [6] 40, 169 (1920).

<sup>13</sup> Debye and Scherrer, *Physik. Z.*, 18, 291 (1917).

<sup>14</sup> Hull, *Phys. Rev.*, [2] 17, 42 (1921).

much greater owing to the fact that oxide ions have been introduced into the lattice. Actually, it is considerably less, 3.32 Å. U.<sup>15</sup> This difference amounts to 0.61 Å. U. The calcium atoms must be considered to have a radius at least 16% less in the oxide than in the metal. Since, in all probability, the metallic calcium atoms have 2 outer electrons which, in the oxide, have gone over to the oxygen atom, some such difference might have been expected. In spite of these drawbacks, however, Bragg's values for atomic radii do give rather good average agreement with the existing data, when they are applied to the distances between *unlike atoms of compounds*, if these atoms are adjacent in the crystal.

Evidence that the type of lattice must in certain cases be taken into account, is furnished by the results of Wilsey on the silver halides.<sup>9</sup> Wilsey has found that silver chloride and bromide are simple cubic whereas the iodide crystallizes in the diamond type of lattice. The distances between nearest unlike atoms are, silver chloride 2.78 Å. U.; silver bromide 2.89 Å. U.; silver iodide 2.83 Å. U. The distance between silver and iodide ions is a little less than the distance between silver and bromide ions, although it is almost certain that the iodine atom is larger than the bromine atom. Clearly, it is due to the distinctive type of packing in the silver iodide crystal that the iodide ions appears to be the smaller.

The domain of an atom in a crystal in all probability depends on its state of combination, that is to say, on the number and the arrangement of electrons in its outer shell, as well as on the kind of atom concerned, and, in certain cases, on the arrangement of atoms in the crystal. Bragg assumes that everything but the kind of atom can be left out of account. The author, on the other hand, suggests that the particular kind of atom is unimportant, *for atoms of the same rare-gas type*, and that the contribution of an atom to the distance between it and another atom in a crystal depends upon the number and arrangement of electrons about its positive nucleus, upon the type of lattice, at least as this affects the latter, and, ordinarily, upon the charge carried by the atom. Apparently, the latter is sometimes also unimportant when the atoms are close-packed, as in the case of substances crystallizing in the diamond lattice (*e. g.*, zinc sulfide and cuprous chloride).

Davey has recently analyzed the inter-atomic distances in the alkali halides from this point of view with success.<sup>16</sup> This series and the series of substances crystallizing in the diamond lattice are the only ones sufficiently developed at the present time to allow of analysis.

### Summary

As an alternative to W. L. Bragg's view that the distances between

<sup>15</sup> Davey and Hoffman, *Phys. Rev.*, [2] 15, 333 (1920).

<sup>16</sup> Davey, *ibid.*, [2] 18, 102 (1921).

atoms in crystals can be expressed in terms of atomic radii characteristic only of the element concerned, it is suggested that the particular element is of secondary importance, *for elements whose atoms are of the same rare-gas type*, and that the contribution of an atom to the distance between it and another atom in a crystal depends upon the number and arrangement of electrons about its positive nucleus, upon the type of lattice, at least as this affects the latter, and, ordinarily, upon the magnitude of the charge carried by the atom.

The inter-atomic distances in substances crystallizing in the diamond type of lattice have been analyzed from this point of view.

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[CONTRIBUTION FROM THE GATES CHEMICAL LABORATORY, CALIFORNIA INSTITUTE OF TECHNOLOGY, No. 11]

## THE CRYSTAL STRUCTURES OF COMPLEX CYANIDES OF POTASSIUM WITH ZINC, CADMIUM AND MERCURY

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### I. Introduction

The complex cyanides  $K_2Zn(CN)_4$ ,  $K_2Cd(CN)_4$ ,  $K_2Hg(CN)_4$ ,  $Tl_2Zn(CN)_4$ , and  $Tl_2Hg(CN)_4$  are mentioned by Groth<sup>2</sup> as probably crystallizing with cubic symmetry; but apparently only the first compound has been shown to be optically isotropic. In the work to be here described crystals of the first three of these compounds were prepared and found to be optically isotropic. Their structures were also determined by X-ray methods. The relation of the new structures to those of some other crystals, as well as the magnitude of the interatomic distances, present some interesting features which will be pointed out in the latter part of this article.

### II. Materials and Methods of Experimentation

Potassium zinc cyanide was prepared by adding a solution of potassium cyanide (imported "sodium free" potassium cyanide was used throughout) to zinc sulfate solution, washing the precipitate, and dissolving it in warm, conc. potassium cyanide solution, from which the product separated on cooling.

Potassium cadmium cyanide was prepared by adding ammonium hydroxide to cadmium nitrate solution, washing the precipitate, and dissolving it in potassium cyanide solution.

Potassium mercury cyanide was obtained by adding mercuric oxide to potassium cyanide solution, and recrystallizing the product.

In all cases the crystals used were obtained by slow evaporation of their aqueous

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<sup>2</sup> Groth, "Chemische Krystallographie," Engelmann, Leipzig, 1906. Vol. 1, p. 334, ff.

solutions at room temperature; this method readily gave crystals 1 sq. cm. or more in cross section. They were octahedral in habit. No definite cleavage was observed.

The densities of the crystals were determined on small specimens by the Retgers suspension method. They were found to be:  $K_2Zn(CN)_4$ , 1.673;  $K_2Cd(CN)_4$ , 1.847;  $K_2Hg(CN)_4$ , 2.434.

The X-ray data were obtained in two ways: (1) from spectrographic measurements of the characteristic rays from a rhodium target, using calcite as a reference crystal; (2) from unsymmetrical Laue photographs. As the apparatus and routine parts of the treatment of the data were substantially the same as those previously used,<sup>3</sup> no further description of the apparatus or restatement of formulas used will be given.

### III. Spectral Photographic Data

In Tables I, II and III are given the angles of reflection of the rhodium lines  $\beta=0.5453 \text{ \AA.}$  and  $\alpha=0.614 \text{ \AA.}$  (the doublet being not completely resolved), and the estimated intensities of the reflections.

To get the number of molecules  $m$  in the unit of structure, the strongest reflection from the (111) face may conveniently be used. If  $n$  is the order of reflection, the values of  $n^3/m$  are found in the usual way to be:  $K_2Zn(CN)_4$ , 3.355;  $K_2Cd(CN)_4$ , 3.35;  $K_2Hg(CN)_4$ , 3.365. From this it follows that  $m = 8$ , and for this reflection  $n = 3$ , which gives  $n^3/m = 3.365$ . The order of each other reflection may readily be shown to have the value given in the fourth column of the tables. The value of  $d_{100}$ , the length of the unit of structure, calculated from each reflection, is given in the fifth column.

TABLE I  
REFLECTION DATA FOR POTASSIUM ZINC CYANIDE

Plane	Line	Observed angle of reflection	$n$	$d_{100}$	Intensity	$\sqrt{A^2 + B^2}$
(111)	$\alpha$	$2^\circ 27'$	1	(12.4)	faint	35
			2		absent	30
	$\beta$	$6^\circ 29'$	3	12.54		
	$\alpha$	$7^\circ 19'$	3	12.52	medium	342
	$\alpha$	$9^\circ 47'$	4	12.52	very weak	229
(100)	$\alpha$	$12^\circ 16'$	5	12.51	weak	334
	$\beta$	$4^\circ 59'$	4	12.55		
	$\alpha$	$5^\circ 37'$	4	12.55	medium	365
	$\beta$	$10^\circ 3'$	8	12.50		
	$\alpha$	$11^\circ 18'$	8	12.53	medium	569
(110)	$\beta$	$3^\circ 31'$	2	12.57		
	$\alpha$	$3^\circ 58'$	2	12.55	medium strong	297
	$\beta$	$7^\circ 1'$	4	12.61		
	$\alpha$	$7^\circ 57'$	4	12.56	very strong	764
	$\beta$	$10^\circ 37\frac{1}{2}'$	8	12.54		
	$\alpha$	$11^\circ 59'$	8	12.56	medium	572
Mean				12.54		
Calc. from density				12.50 $\text{\AA.}$		

<sup>3</sup> Dickinson, THIS JOURNAL, 44, 276 (1922).



TABLE II  
REFLECTION DATA FOR POTASSIUM CADMIUM CYANIDE

Plane	Line	Observed angle of reflection	$n$	$d_{100}$	Intensity	$\sqrt{A^2 + B^2}$
(111)	$\alpha$	2° 21'	1	(13.0—)	weak	137
			2		absent	30
	$\beta$	6° 20'	3	12.84		
	$\alpha$	7° 8'	3	12.85	medium	444
			4		absent	85
	$\alpha$	11° 57'	5	12.84	weak	436
			Mean		12.84	
	Calc. from density				12.81 Å.	

TABLE III  
REFLECTION DATA FOR POTASSIUM MERCURY CYANIDE

Plane	Line	Observed angle of reflection	$n$	$d_{100}$	Intensity	$\sqrt{A^2 + B^2}$
(111)	$\alpha$	2° 24'	1	(12.7)	weak	318
			2		absent	30
	$\beta$	6° 22½'	3	12.76		
	$\alpha$	7° 11'	3	12.77	medium	625
	$\alpha$	9° 36'	4	12.75	very weak	171
	$\alpha$	12° 1'	5	12.77	weak	617
			Mean	12.76		
		Calc. from density	12.75 Å.			

#### IV. Application of the Theory of Space Groups

The simple requirement that there shall be 8 molecules in the unit still leaves as possible a considerable variety of structures. The additional assumption, however, that all the atoms of each element are situated in equivalent positions in the structure limits the possibilities to those space groups which can give 8, 16, 32, and 32 equivalent positions. These space groups are:<sup>4</sup>  $T_h^4$ ,  $O_h^4$ ,  $O_h^7$ . Each of these leads to the same possible arrangements of atoms; and it will be shown that a structure can be derived from them that is in satisfactory accord with the experimental data.

The possible positions for the atoms are:

K: I  $(\frac{1}{2}\frac{1}{2}\frac{1}{2})$   $(\frac{1}{2}\frac{1}{2}\frac{1}{2})$   $(\frac{1}{2}\frac{1}{2}\frac{1}{2})$   $(\frac{1}{2}\frac{1}{2}\frac{1}{2})$   $(\frac{1}{2}\frac{1}{2}\frac{1}{2})$   $(\frac{1}{2}\frac{1}{2}\frac{1}{2})$   $(\frac{1}{2}\frac{1}{2}\frac{1}{2})$   $(\frac{1}{2}\frac{1}{2}\frac{1}{2})$   
 $(\frac{1}{2}\frac{1}{2}\frac{1}{2})$   $(\frac{1}{2}\frac{1}{2}\frac{1}{2})$   $(\frac{1}{2}\frac{1}{2}\frac{1}{2})$   $(\frac{1}{2}\frac{1}{2}\frac{1}{2})$   $(\frac{1}{2}\frac{1}{2}\frac{1}{2})$   $(\frac{1}{2}\frac{1}{2}\frac{1}{2})$   $(\frac{1}{2}\frac{1}{2}\frac{1}{2})$   $(\frac{1}{2}\frac{1}{2}\frac{1}{2})$

or II  $(\frac{1}{2}\frac{1}{2}\frac{1}{2})$   $(\frac{1}{2}\frac{1}{2}\frac{1}{2})$   $(\frac{1}{2}\frac{1}{2}\frac{1}{2})$   $(\frac{1}{2}\frac{1}{2}\frac{1}{2})$   $(\frac{1}{2}\frac{1}{2}\frac{1}{2})$   $(\frac{1}{2}\frac{1}{2}\frac{1}{2})$   $(\frac{1}{2}\frac{1}{2}\frac{1}{2})$   $(\frac{1}{2}\frac{1}{2}\frac{1}{2})$   
 $(\frac{1}{2}\frac{1}{2}\frac{1}{2})$   $(\frac{1}{2}\frac{1}{2}\frac{1}{2})$   $(\frac{1}{2}\frac{1}{2}\frac{1}{2})$   $(\frac{1}{2}\frac{1}{2}\frac{1}{2})$   $(\frac{1}{2}\frac{1}{2}\frac{1}{2})$   $(\frac{1}{2}\frac{1}{2}\frac{1}{2})$   $(\frac{1}{2}\frac{1}{2}\frac{1}{2})$   $(\frac{1}{2}\frac{1}{2}\frac{1}{2})$

Zn:III (000)  $(\frac{1}{2}\frac{1}{2}0)$   $(\frac{1}{2}0\frac{1}{2})$   $(0\frac{1}{2}\frac{1}{2})$   $(\frac{1}{2}\frac{1}{2}\frac{1}{2})$   $(\frac{1}{2}\frac{1}{2}\frac{1}{2})$   $(\frac{1}{2}\frac{1}{2}\frac{1}{2})$   $(\frac{1}{2}\frac{1}{2}\frac{1}{2})$   $(\frac{1}{2}\frac{1}{2}\frac{1}{2})$

or IV  $(\frac{1}{2}\frac{1}{2}\frac{1}{2})$   $(00\frac{1}{2})$   $(0\frac{1}{2}0)$   $(\frac{1}{2}00)$   $(\frac{1}{2}\frac{1}{2}\frac{1}{2})$   $(\frac{1}{2}\frac{1}{2}\frac{1}{2})$   $(\frac{1}{2}\frac{1}{2}\frac{1}{2})$   $(\frac{1}{2}\frac{1}{2}\frac{1}{2})$

C: V  $(uuu)$   $(\frac{1}{2}+u, \frac{1}{2}+u, u)$   $(\frac{1}{2}+u, u, \frac{1}{2}+u)$   $(u, \frac{1}{2}+u, \frac{1}{2}+u)$   
 $(u\bar{u}\bar{u})$   $(\frac{1}{2}+u, \frac{1}{2}-u, \bar{u})$   $(\frac{1}{2}+u, \bar{u}, \frac{1}{2}-u)$   $(u, \frac{1}{2}-u, \frac{1}{2}-u)$   
 $(\bar{u}u\bar{u})$   $(\frac{1}{2}-u, \frac{1}{2}+u, \bar{u})$   $(\frac{1}{2}-u, u, \frac{1}{2}-u)$   $(\bar{u}, \frac{1}{2}+u, \frac{1}{2}-u)$   
 $(\bar{u}\bar{u}u)$   $(\frac{1}{2}-u, \frac{1}{2}-u, u)$   $(\frac{1}{2}-u, \bar{u}, \frac{1}{2}+u)$   $(\bar{u}, \frac{1}{2}-u, \frac{1}{2}+u)$

<sup>4</sup> Niggli, "Geometrische Krystallographie des Diskontinuums," Bornträger, Leipzig, 1919, p. 410; also *Phys. Zeit.*, 19, 229 (1918).

$(\frac{1}{2}-u, \frac{1}{2}-u, \frac{1}{2}-u)$   $(\frac{3}{2}-u, \frac{3}{2}-u, \frac{1}{2}-u)$   $(\frac{3}{2}-u, \frac{1}{2}-u, \frac{3}{2}-u)$   $(\frac{1}{2}-u, \frac{3}{2}-u, \frac{3}{2}-u)$   
 $(\frac{1}{2}-u, \frac{1}{2}+u, \frac{1}{2}+u)$   $(\frac{3}{2}-u, \frac{3}{2}+u, \frac{1}{2}+u)$   $(\frac{3}{2}-u, \frac{1}{2}+u, \frac{3}{2}+u)$   $(\frac{1}{2}-u, \frac{3}{2}+u, \frac{3}{2}+u)$   
 $(\frac{1}{2}+u, \frac{1}{2}-u, \frac{1}{2}+u)$   $(\frac{3}{2}+u, \frac{3}{2}-u, \frac{1}{2}+u)$   $(\frac{3}{2}+u, \frac{1}{2}-u, \frac{3}{2}+u)$   $(\frac{1}{2}+u, \frac{3}{2}-u, \frac{3}{2}+u)$   
 $(\frac{1}{2}+u, \frac{1}{2}+u, \frac{1}{2}-u)$   $(\frac{3}{2}+u, \frac{3}{2}+u, \frac{1}{2}-u)$   $(\frac{3}{2}+u, \frac{1}{2}+u, \frac{3}{2}-u)$   $(\frac{1}{2}+u, \frac{3}{2}+u, \frac{3}{2}-u)$

N: VI A similar set of coördinates in v.

It is to be noted that all *distinct* combinations of the above coördinates are obtained by combining V, VI, and either I or II with III; and by giving  $u$  and  $v$  any independent values between  $\frac{1}{8}$  and  $\frac{5}{8}$ . Either of these combinations can be shown to have the following properties: for the plane (100) all reflections except the 4th, 8th... orders must be absent; for the plane (110), all odd orders must be absent; for (111) any order may be present. This agrees with the observations.

A treatment of the possibilities arising from complete independence of  $u$  and  $v$  is laborious, and from a practical point of view unnecessary, since the carbon and nitrogen atoms may safely be assumed to be closely associated. Thus the sum of the radii assigned by Bragg<sup>5</sup> to carbon and nitrogen is 1.42 Å.; and Bozorth<sup>6</sup> obtained best agreement in the case of potassium cyanide by placing the carbon and nitrogen 1.15 Å. apart. It therefore seems safe to assume that the distance of the carbon from the nitrogen lies between 1 and 1.5 Å., which is equivalent to assuming that

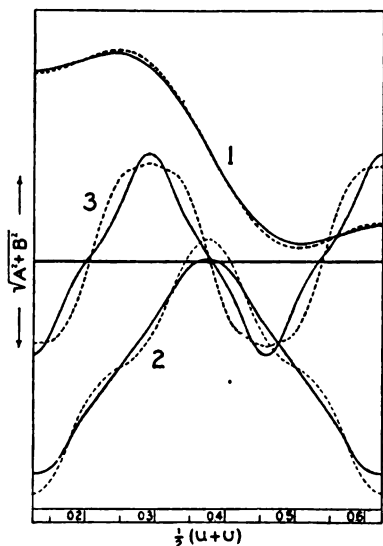


Fig. 1.—Values  $\sqrt{A^2 + B^2}$  for the first three orders from  $K_2Zn(CN)_4$ , (111); the abscissas are  $\frac{1}{2}(u+v)$ . The potassium atoms have Arrangement I.

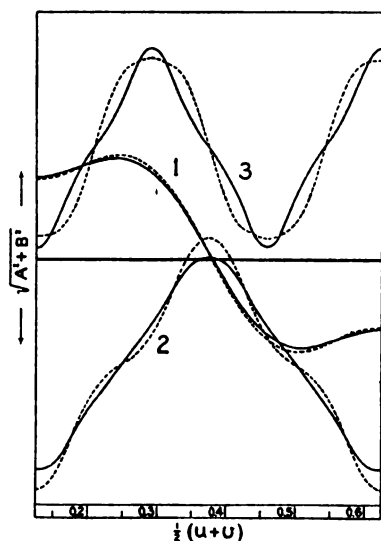


Fig. 2.—Values of  $\sqrt{A^2 + B^2}$  for the first three orders from  $K_2Zn(CN)_4$ , (111); the abscissas are  $\frac{1}{2}(u+v)$ . The potassium atoms have Arrangement II.

<sup>5</sup> Bragg, *Phil. Mag.*, **40**, 180 (1920).

<sup>6</sup> Bozorth, *THIS JOURNAL*, **44**, 317 (1922).

in the zinc compound,  $u$  differs from  $v$  by not less than 0.046 and not more than 0.069.

The intensities of the first three orders of reflection from (111) afford a means of discriminating between the two possible locations of the potassium atoms, and of locating the cyanide group approximately without employing any quantitative assumption of the "normal decline" of intensity. In Figs. 1 and 2 are shown the values of  $\sqrt{A^2 + B^2}$  for the (111) reflections from  $K_2Zn(CN)_4$  calculated in the usual manner. The reflecting powers of the atoms have been taken proportional to the atomic numbers, except for carbon and nitrogen, whose reflecting powers have each been taken proportional to 6.5, instead of to 6 and 7, respectively, since it does not seem possible to distinguish these two atoms. In Fig. 1 the potassium atoms have the arrangement I, and in Fig. 2 the arrangement II. The abscissas,  $\frac{1}{2}(u + v)$ , are positions of a point half-way between the centers of the carbon and nitrogen atoms. The solid curves are for a distance of 1.5 Å. between carbon and nitrogen, and the dotted curves for a distance of 1.0 Å. The only positions where the second order has a small ordinate while the third is much larger than the first, as the observed intensities evidently require, are in Fig. 2 in the neighborhood of  $\frac{1}{2}(u + v) = 0.375$ . It is concluded, then, that the potassium atoms have the positions given by II and that  $\frac{1}{2}(u + v)$  is about  $\frac{3}{8}$ . This structure is capable of accounting for the other abnormalities of the spectra in the same manner. In the last column of Tables I, II and III are given the values of  $\sqrt{A^2 + B^2}$  calculated by placing  $u = 0.34$  and  $v = 0.40$  with the potassium atoms in Position II. On any face where stronger reflections occur at larger angles, the value of the factor  $\sqrt{A^2 + B^2}$  is greater; and where the reflections are weak at small angles, the value of the factor is small.

## V. The Laue Photographic Data

Unsymmetrical Laue photographs were made with  $K_2Zn(CN)_4$ , using slips of crystal approximately parallel to (100) and to (111); while with  $K_2Cd(CN)_4$  and  $K_2Hg(CN)_4$  the X-ray beam was only passed approximately perpendicular to (111). As over a thousand spots were examined, a tabulation of the complete data is impracticable. A number of useful and representative spots have been chosen from each of three photographs; and the indices, estimated intensities, spacings of planes, and values of  $n\lambda$  for these are given in Tables IV, V and VI. The nature of the change of intensity with wavelength is shown by the inclusion of several planes of one form.

The expressions for  $A$  and  $B$  for cases which will be considered can be simplified to the following.

## A. Two indices even.

For  $n=1$ ,  $A=0$ , and  $B=0$ .For  $n=2$ ,  $A=0$ , and  $B=8\Sigma(\bar{C} \sin 4\pi S_n u + \bar{N} \sin 4\pi S_n v)$ 

## B. One index even.

For  $n=1$ ,  $A=0$ , and  $B=0$ .For  $n=2$ ,  $A=8\bar{Z}_n + 8\Sigma(\bar{C} \cos 4\pi S_n u + \bar{N} \cos 4\pi S_n v)$  and  $B=0$ .C. All indices odd, and  $n=1$ .

$$A=4\bar{Z}_n + 4\Sigma \left[ \pm \bar{K} \cos \frac{\pi S_n}{4} + \bar{C} \left( \cos 2\pi S_n u + \cos 2\pi \left( \frac{S_1}{4} - S_n u \right) \right) \right. \\ \left. + \bar{N} \left( \cos 2\pi S_n v + \cos 2\pi \left( \frac{S_1}{4} - S_n v \right) \right) \right] \\ B=4\Sigma \left[ \bar{Z}_n \sin \frac{\pi S_n}{2} \pm \bar{K} \sin \frac{\pi S_n}{4} + \bar{C} \left( \sin 2\pi S_n u + \sin 2\pi \left( \frac{S_1}{4} - S_n u \right) \right) \right. \\ \left. + N \left( \sin 2\pi S_n v + \sin 2\pi \left( \frac{S_1}{4} - S_n v \right) \right) \right]$$

where  $h+k+l=S_1$ ;  $h-k-l=S_2$ ;  $-h+k-l=S_3$ ;  $-h-k+l=S_4$ . The summations are in all cases to be taken from  $n=1$ , to  $n=4$ . The sign before the  $\bar{K}$  term is plus if the potassium atoms have Arrangement I, and minus if they have Arrangement II.

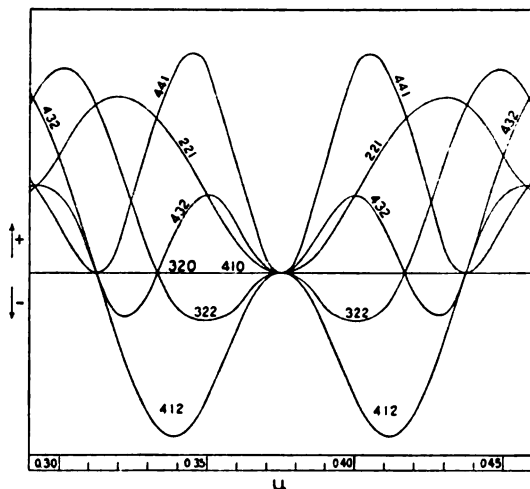


Fig. 3.—Values of  $\Sigma \sin 4\pi S_n u$  for various planes of Class A.

These equations show that planes having any even index may in general reflect in the second, but not in the first order, and that planes having all odd indices may reflect in the first order. The observations are in agreement with these requirements.

Second order reflections from planes of Class A should be due to the cyanide group alone. Planes of this class having one index zero should not

appear in the second order for any values of  $u$  and  $v$ ; and in fact on the photographs none were found, although some were shown to be favorably situated for reflection. The spots of Class A which did appear in the second order are particularly useful in confirming the location of the cyanide group. A consideration of the data of Tables IV, V and VI and of other similar data shows that for all three salts the following relations must be true of the values of  $\sqrt{A^2 + B^2}$ : (441) must be greater than (322) and (432); (421) must be much greater than (322); (221) must be appreciable. The values of  $\sum \sin 4\pi S_n u$  for these planes are shown plotted against values of  $u$  in Fig. 3. The functions defining these curves have the property that if two atoms of equal reflecting power are placed at two different values of the parameter, the resulting value of  $\sqrt{A^2 + B^2}$  will be given by the algebraic sum of the corresponding ordinates. The conditions given above are well satisfied by placing one of the two atoms at 0.34 and the other at 0.40 as in the previous calculations; but the presence of two parameters makes a close determination of their values impossible without resort to rather doubtful quantitative assumptions.

The planes having all odd indices may be further divided into two classes. Class  $C_a$  comprises those which have either only one or all three indices equal to  $8p \pm 3$  (where  $p$  is an integer which need not be the same for each index); and class  $C_b$ , those which have either only one or all three indices equal to  $8p \pm 1$ . Examples of  $C_a$  are (157), (355), (951); examples of  $C_b$  are: (513), (573), (771). When planes of about the same spacing were compared, it was found that those of Class  $C_a$  were distinctly more intense than those of  $C_b$ ; the intensity difference was greatest with the zinc salt and least with the mercury salt. Neglecting for the moment the cyanide group, the expression for  $\sqrt{A^2 + B^2}$  reduces to  $4\sqrt{2}Zn - 8\bar{K}$  for Class  $C_a$  and to  $4\sqrt{2}Zn + 8\bar{K}$  for Class  $C_b$  if the potassium atoms have Arrangement I, and *vice versa* if they have Arrangement II. There is thus a wide range of new evidence for Arrangement II. This conclusion is not invalidated by the neglect of the cyanide group; for if  $v - \frac{3}{8} = \frac{3}{8} - u$  and the carbon and nitrogen reflect equally the  $\bar{C}$  and  $\bar{N}$  terms become zero. The fact that abnormalities in the intensity relations among the planes of class  $C_a$  alone or  $C_b$  alone were certainly small is taken to indicate that  $u$  and  $v$  have approximately such values; this test is especially sensitive in the case of Class  $C_b$  of the zinc compound where the resultant of the zinc and potassium reflections is small.

By careful direct comparison of planes of the same class the following intensity differences in the case of the zinc salt were shown: (951) > (773), (975) > (11.5.3), (553) > (731), (771) > (753). The differences were small with the zinc salt and very uncertain with the others. The parameters  $u = 0.34$  and  $v = 0.40$  account for these.

Planes of Class B also showed very slight abnormalities. With the zinc salt it seemed clear that  $\sqrt{A^2 + B^2}$  should stand in the order (501)

TABLE IV  
LAUE PHOTOGRAPHIC DATA FROM  $K_2Zn(CN)_4$

Plane	Estimated intensity	Spacing	$n\lambda$	Plane	Estimated intensity	Spacing	$n\lambda$
(122)	1.8	4.18	0.88	(753)	0.05	1.38	0.55
(023)	0.0	3.48	0.82	(913)	1.6	1.32	0.55
(223)	0.1	3.04	0.84	(771)	0.4	1.26	0.46
(214)	0.5	2.74	0.80	(951)	1.2	1.21	0.38
(124)	0.1	2.74	0.60	(915)	1.4	1.21	0.50
(432)	0.05	2.33	0.95	(377)	1.3	1.21	0.48
(441)	0.3	2.18	0.96	(975)	0.8	1.01	0.42
(414)	0.2	2.18	0.80	(579)	0.9	1.01	0.48
(133)	0.8	2.88	0.52	(3·11·5)	0.7	1.01	0.48
(313)	1.4	2.88	0.98	(1·11·7)	0.1	0.96	0.55
(315)	0.4	2.12	0.55	(11·3·7)	0.05	0.94	0.46
(355)	6.	1.63	0.44	(599)	0.2	0.92	0.43
(731)	2.	1.63	0.36	(411)	3.	2.96	0.98
(713)	5.	1.63	0.43	(233)	0.8	2.67	0.81
(137)	4.	1.63	0.67	(134)	0.9	2.46	0.77
(317)	1.4	1.63	0.81	(413)	1.2	2.46	0.84
(713)	0.3	1.63	0.99	(125)	0.7	2.29	0.89
(373)	0.4	1.53	0.54	(415)	0.4—	1.94	0.95
(157)	3.5	1.45	0.40	(163)	0.2—	1.85	0.96
(571)	3.	1.45	0.55	(534)	0.2—	1.77	0.94
(735)	0.1+	1.38	0.44	(037)	0.1+	1.65	0.85

TABLE V  
LAUE PHOTOGRAPHIC DATA FROM  $K_2Cd(CN)_4$

Plane	Estimated intensity	Spacing	$n\lambda$	Plane	Estimated intensity	Spacing	$n\lambda$
(221)	0.6	4.28	0.87	(159)	0.7	1.24	0.41
(032)	0.0	3.56	0.92	(915)	0.4	1.24	0.87
(223)	0.2	3.11	1.04	(377)	0.6	1.24	0.42
(124)	0.1	2.80	0.64	(757)	0.5	1.16	0.41
(412)	0.4	2.80	1.20	(3·11·3)	0.3	1.09	0.40
(342)	0.0	2.38	0.86	(1·5·11)	0.1	1.06	0.48
(441)	0.1+	2.23	0.84	(11·5·3)	0.6	1.03	0.47
(135)	0.8	2.17	0.40	(597)	0.3	1.03	0.40
(513)	1.6	2.17	0.79	(1·11·7)	0.1	0.98	0.38
(335)	9.	1.96	0.45	(11·9·1)	0.1	0.90	0.38
(155)	0.7	1.80	0.41	(5·1·15)	0.1	0.81	0.47
(553)	4.	1.67	0.45	(332)	0.7	2.74	0.86
(535)	2.	1.67	0.90	(314)	0.7	2.52	0.78
(571)	1.0	1.48	0.34	(215)	0.4	2.34	0.81
(715)	1.8	1.48	0.43	(125)	0.6	2.34	0.92
(751)	6.	1.48	0.48	(053)	0.2—	2.20	0.72
(175)	5.	1.48	0.53	(035)	0.2	2.20	0.92
(751)	1.5	1.48	0.86	(145)	0.2	1.98	0.82
(573)	0.2+	1.41	0.39	(453)	0.1	1.82	0.85
(771)	0.2	1.29	0.38	(370)	0.1	1.69	0.76

TABLE VI  
LAUE PHOTOGRAPHIC DATA FROM  $K_2Hg(CN)_4$

Plane	Estimated intensity	Spacing	$n\lambda$	Plane	Estimated intensity	Spacing	$n\lambda$
( $\bar{2}21$ )	0.6	4.25	1.24	(917)	0.6	1.11	0.35
(032)	0.0	3.54	0.74	( $\bar{5}\cdot 11\cdot \bar{1}$ )	0.4	1.05	0.37
(223)	0.0	3.10	0.69	( $\bar{3}\cdot \bar{5}\cdot 11$ )	0.8	1.02	0.36
( $\bar{2}14$ )	0.3	2.78	0.79	(779)	0.2	0.95	0.34
(124)	0.3	2.78	0.90	(959)	0.3	0.93	0.35
(342)	0.0	2.37	0.80	( $\bar{3}\cdot 13\cdot \bar{3}$ )	0.4	0.93	0.44
(441)	0.05	2.22	0.71	( $\bar{1}\cdot 13\cdot \bar{5}$ )	0.2	0.91	0.42
(315)	7.	2.16	0.48	(13·5·3)	0.3	0.90	0.43
(155)	3.	1.79	0.48	(332)	1.2	2.72	1.10
(733)	3.	1.56	0.33	(143)	3.5	2.50	0.89
(157)	4.	1.47	0.33	(413)	0.9	2.50	1.13
(751)	5.	1.47	0.35	(152)	2.5	2.33	0.69
(175)	6.	1.47	0.43	(215)	0.7	2.33	1.07
(517)	1.2	1.47	0.57	(433)	1.5	2.19	0.70
(715)	1.0	1.47	0.60	(305)	1.3	2.19	0.88
(375)	1.6	1.40	0.35	(514)	0.9	1.97	0.71
(755)	1.1	1.28	0.35	(271)	0.3	1.73	0.88
(519)	2.0	1.23	0.44	(073)	0.3	1.68	0.83
(737)	1.8	1.23	0.36				

$>(431)>(332)$  for these three planes. The parameters cited account for this order but would lead one to expect larger intensity differences than were observed. If it is attempted to improve the agreement by taking other values of  $u$  and  $v$  (e. g., by placing the carbon and nitrogen atoms much closer together near 0.375) the qualitative account of the spectrographic intensities fails. The difficulty is of the same character as that found by Bozorth with potassium cyanide and is removed in both cases if atoms of the cyanide group reflect the less strongly relative to the other atoms, the smaller the spacing of the planes,<sup>7</sup> so that while qualitative agreement can be obtained using atomic numbers with the simple planes giving the spectrographic data, greater difficulty is found with the complicated planes of the Laue photographs.

However, the various tests which have been applied to the Laue photographic data without resort to assumptions concerning the reflecting powers justify beyond much doubt the conclusions that the potassium atoms have Arrangement II; the zinc, cadmium, or mercury atoms Arrangement III; and the carbon and nitrogen atoms Arrangement V and VI with  $\frac{1}{2}(u + v)$  equal to about 0.37.

## VI. Discussion of the Crystal Structures

The arrangement of the zinc, cadmium, or mercury atoms is shown by the large cube of Fig. 4 in which BG is equal to  $d_{100}$ . The arrangement

<sup>7</sup> Increasing departure from proportionality with atomic number with decreasing plane spacing in the case of NaCl is indicated by spectrometer measurements; W. L. Bragg, James, and Bosanquet, *Phil. Mag.*, **41**, 316 (1921).

of the other atoms is shown by the small cubes in the lower part of the figure. The structure may be obtained by the alternation of the small cubes in the manner indicated by the lettering.

There is good evidence<sup>8</sup> that in solution the ions  $\text{Zn}(\text{CN})_4^-$ ,  $\text{Cd}(\text{CN})_4^-$ , and  $\text{Hg}(\text{CN})_4^-$  exist. One may well inquire whether there is evidence as to the existence of these ions in the solid state. In answer to this it may be pointed out that each cyanide group is situated differently with respect to some one zinc atom from what it is with respect to any other; and that each zinc atom has four cyanide groups surrounding it and identically related to it. No similar remarks apply to the potassium atoms. The atoms can accordingly be segregated into  $\text{Zn}(\text{CN})_4$  groups and K atoms without resorting to arbitrary selection.

On the other hand, it is remarkable that the structure of these complex cyanides is of the same type as that previously found<sup>9</sup> for spinel,  $\text{MgAl}_2\text{O}_4$ , and magnetite,  $\text{Fe}_3\text{O}_4$ . The cyanide group has taken the place of the oxygen atoms, the potassium the place of the aluminum or ferric iron, and the zinc the place of the magnesium or ferrous iron. The crystal structure evidence is, therefore, as much indicative of  $\text{FeO}_4$  groups and  $\text{MgO}_4$  groups as of  $\text{Zn}(\text{CN})_4$  groups; but there seems to be little

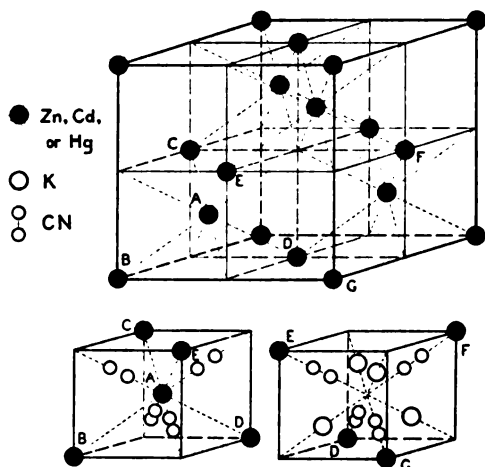


Fig. 4.—Arrangement of the atoms in  $\text{K}_2\text{Zn}(\text{CN})_4$ ,  $\text{K}_2\text{Cd}(\text{CN})_4$ , or  $\text{K}_2\text{Hg}(\text{CN})_4$ .

chemical evidence of the existence of  $\text{MgO}_4$  groups. If the likeness of crystal structure in the two classes of compounds is taken as evidence of correspondence of chemical affinities,<sup>10</sup> either the  $\text{MgO}_4$  group must be accepted or the  $\text{Zn}(\text{CN})_4$  group given up, in the crystalline state. It is plausible to assume that in the solid state the groups are themselves completely ionized into  $\text{Mg}^{++}$  and  $\text{O}^-$  ions and into  $\text{Zn}^{++}$  and  $\text{CN}^-$  ions.

The values of  $d_{100}$  as well as the distance from the center of the cyanide group (whose position is probably more accurately known than the po-

<sup>8</sup> Abegg, "Handbuch der Anorganische Chemie," Hirzel, Leipzig, 1905, II, 2, pp. 384, 500, 650.

<sup>9</sup> W. H. Bragg, *Phil. Mag.*, 30, 305 (1915). Nishikawa, *Proc. Tokyo Math. Phys. Soc.*, 8, 199 (1915).

<sup>10</sup> The lack of definite cleavage in both series of crystals lends some support to this view.



sitions of the individual carbon and nitrogen atoms) are summarized in Table VII. It will be noticed that the cadmium compound is not intermediate between the zinc and mercury compounds, but is built on a slightly larger scale than even the mercury compound. It will also be seen that, since the potassium atoms are situated relatively to the cyanide groups substantially as in potassium cyanide,<sup>6</sup> the distances between their centers in each case may properly be compared. The agreement is surprisingly close; indeed, if the bivalent atoms of the complex cyanide are simply removed and replaced by twice as many potassium atoms in the proper position, the structure of potassium cyanide is almost quantitatively reproduced.

TABLE VII  
DISTANCES

Substance	$d_{100}$	K to CN	Zn, Cd, or Hg to CN
$K_2Zn(CN)_4$	12.54 Å.	3.20 Å.	2.61 Å.
$K_2Cd(CN)_4$	12.84	3.28	2.67
$K_2Hg(CN)_4$	12.76	3.25	2.65
KCN	$\frac{1}{2} \times 13.10$	3.28	..

### VII. Summary

By means of spectral photographs and unsymmetrical Laue photographs, the structures of  $K_2Zn(CN)_4$ ,  $K_2Cd(CN)_4$  and  $K_2Hg(CN)_4$  have been determined. In the interpretation of the data the highly useful theory of space-groups has been employed, and it was not necessary to make any quantitative assumptions as to the "normal decline" of intensity. The results show that these compounds have the structure summarized at the end of Section V, represented by Fig. 4, and discussed in Section VI. A remarkable fact is that these complex cyanides have the same structure as magnetite ( $Fe_3O_4$ ) and spinel ( $MgAl_2O_4$ ).

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### NOTE

**A Simple Formula for the Calculation of the Specific Heats of Solids.**—The most important present day theories for the specific heat of solids agree in one respect, namely, that for a large class of solids,  $C_v$  is the same function of the temperature, divided by a constant which is characteristic of the substance. In other words

$$C_v = f\left(\frac{T}{\theta}\right) \quad (1)$$

where  $T$  is the absolute temperature,  $\theta$  is the characteristic temperature for each substance and  $f$  has the same form for all the substances under consideration. This is Equation 5 in the treatment of specific heats given by Lewis and Gibson.<sup>1</sup>

<sup>1</sup> Lewis and Gibson, THIS JOURNAL, 39, 2558 (1917).

Usually the function  $f$  is very complicated in form; for example, the equations of Einstein, Nernst and Lindemann, and Debye are very difficult to evaluate, while Lewis and Gibson make no attempt to obtain an analytic expression for the form of  $f$ . It is the purpose of this note to present a simple analytic formula which has been found to represent specific heats with sufficient accuracy for many calculations.

**The Specific Heat Formula.**—A simple form of the function of the previous equation which has been found to fit the experimental values is

$$C_p = 2.91 + 2.89 \tanh 2.95 \log \frac{T}{\theta} \quad (2)$$

where  $C_p$  is given in calories per gram-atom. It will readily be seen that Equation 2 is a modification of the equation  $y = \tanh x$  after a transformation of axis. The values of the numerical constants have been adjusted by the method of least squares to the values of  $C_p$  given in Table I of the paper by Lewis and Gibson.<sup>2</sup> No theoretical significance is claimed for Equation 2. It recommends itself, however, because of its analytic simplicity. It is of interest to note that the above formula is symmetrical about the axis  $C_p = \frac{3}{2} R = 2.95$ , while the actual experimental curve is apparently not quite symmetrical.

In the following table the values of  $C_p$  calculated from the above formula are compared with those of Lewis and Gibson. The greatest difference is seen to occur where  $\log \theta$  has the largest negative values, *i. e.*, at the lowest temperatures. The agreement at higher temperatures is well within the experimental error.

TABLE I  
SPECIFIC HEATS

$\log \frac{T}{\theta}$	$C_p$ Calc.	$C_p$ Lewis	$C_p$ Calc. — $C_p$ Lewis	$\log \frac{T}{\theta}$	$C_p$ Calc.	$C_p$ Lewis	$C_p$ Calc. — $C_p$ Lewis
-0.6	0.18	0.11	+0.09	0.4	5.30	5.26	+0.04
-0.5	0.31	0.21	+0.10	0.5	5.51	5.49	+0.02
-0.4	0.52	0.43	+0.09	0.6	5.64	5.65	-0.01
-0.3	0.87	0.84	+0.03	0.7	5.71	5.72	-0.01
-0.2	1.38	1.43	-0.5	0.8	5.74	5.76	-0.02
-0.1	2.08	2.19	-0.11	0.9	5.77	5.78	-0.01
0.0	2.91	2.98	-0.07	1.0	5.78	5.79	-0.01
0.1	3.74	3.78	-0.04	1.1	5.79	5.80	-0.01
0.2	4.44	4.43	+0.01	1.2	5.79	5.81	-0.02
0.3	4.95	4.91	+0.04				

**The Entropy Equation.**—Since the entropy equation is obtained by integration of the specific heat equation we may write

$$S_p = \int \left( 2.91 + 2.89 \tanh 2.95 \log \frac{T}{\theta} \right) d \ln \frac{T}{\theta} \quad (3)$$

<sup>2</sup> Ref. 1, p. 2561.

Evaluating the constant of integration by putting the entropy equal to the Lewis-Gibson value 1.62 when  $\log \frac{T}{\theta} = 0$ , we obtain

$$S_0 = 6.70 \log \frac{T}{\theta} + 5.18 \log \cosh 2.95 \log \frac{T}{\theta} + 1.62. \quad (4)$$

In the following table the calculated entropies are compared with those obtained graphically by Lewis and Gibson.<sup>2</sup> The agreement is good.

TABLE II  
COMPARISON OF ENTROPIES

$\log \frac{T}{\theta}$	$S_0$ Calc.	$S_0$ Lewis	$S_0 - S_0$ Calc.-Lewis	$\log \frac{T}{\theta}$	$S_0$ Calc.	$S_0$ Lewis	$S_0 - S_0$ Calc.-Lewis
-0.6	0.08	0.04	+0.04	+0.4	5.60	5.59	+0.01
-0.5	0.15	0.07	+0.08	+0.5	6.85	6.82	+0.03
-0.4	0.24	0.15	+0.09	+0.6	8.12	8.08	+0.04
-0.3	0.40	0.30	+0.10	+0.7	9.43	9.41	+0.02
-0.2	0.65	0.53	+0.12	+0.8	10.76	10.74	+0.02
-0.1	1.05	0.98	+0.07	+0.9	12.07	12.07	0.00
0.0	1.62	1.62	0.00	+1.0	13.40	13.40	0.00
+0.1	2.39	2.41	-0.02	+1.1	14.74	14.74	0.00
+0.2	3.33	3.37	-0.04	+1.2	16.08	16.08	0.00
+0.3	4.42	4.42	0.00				

**The Method of Calculation.**—The values of  $\tanh$  and  $\log \cosh$  are readily obtained from tables of hyperbolic functions.<sup>3</sup> The remainder of the labor is only in multiplication and addition, the former of which can be carried out with sufficient precision for the purpose with a 20-inch slide rule. In fact all of the calculated values given in the two tables were very readily obtained in this manner.

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<sup>3</sup> The "Smithsonian Mathematical Tables" hyperbolic functions are quite suited for this purpose.

[CONTRIBUTION FROM THE DERMATOLOGICAL RESEARCH INSTITUTE OF PHILADELPHIA]

## ORGANIC NITRO COMPOUNDS CONTAINING MERCURY

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## Introduction

Up to the present day, but very few organic nitro compounds containing mercury attached to nuclear carbon have been described in the scientific literature. Dimroth<sup>1</sup> in 1902 prepared a mercury derivative of nitrobenzene; Hantsch and Auld<sup>2</sup> in 1906 described mercury derivatives of various nitrophenols; in 1911 Bayer and Co.<sup>3</sup> patented the mercury derivatives of 4-chloro-2-nitrophenol; in 1911 and 1912 Blumenthal<sup>4,5,6</sup> prepared the mercury derivative of nitrobenzoic acid. In 1919 Raiziss and Gavron<sup>7</sup> prepared mercury derivatives of 3-nitro-4-hydroxyphenylarsonic acid and 3,5-dinitro-4-hydroxyphenylarsonic acid. Lecher<sup>8</sup> in 1920 prepared mercury-*o*-nitrophenyl-mercaptide; Kharasch and Piccard<sup>9</sup> prepared *p,o,o'*-3-mercuric chloride-dinitro-diphenylamine and also mercury-bis-3-dinitro-mercazine.

Since 1913 one of the authors in collaboration with Drs. J. F. Schamberg and J. A. Kolmer has been engaged in the study of the toxicity and bactericidal effects of organic mercury compounds. During this time a considerable number of such compounds have been investigated by us, many of which had not previously been synthesized. Of this entire number the sodium hydroxymercuri-*o*-nitrophenolate, named by us Mercurophen, exhibited biological properties far superior to any of the others. It has since been investigated by physicians and clinicians,<sup>10,11</sup> and several interesting facts have been established.

The study of mercurophen suggested to us the idea that the nitro group enhances the bactericidal influence of organic mercurials. This is in direct contrast to the theory of Ehrlich who regarded the nitro group as exerting a distherapeutic influence upon organic arsenical compounds. While our experience with the latter class of compounds *in vivo* corroborates Ehrlich's findings, results of experiments *in vitro* are just the reverse.

<sup>1</sup> Dimroth, *Ber.*, 35, 2036 (1902).

<sup>2</sup> Hantsch and Auld, *ibid.*, 39, 1105 (1906).

<sup>3</sup> *Zentr.*, [I] 1769 1911; Ger. pat. 234851.

<sup>4</sup> Blumenthal, *Biochem. Z.*, 32, 59 (1911); *Deut. Med. Wochschr.*, 38, 543 (1912); Ger. pat. 249725.

<sup>5</sup> Blumenthal, *Biochem. Z.*, 39, 50 (1912).

<sup>6</sup> Blumenthal and Oppenheim, *ibid.*, 57, 261 (1913).

<sup>7</sup> Raiziss, Kolmer and Gavron, *J. Biol. Chem.*, 40, 533 (1919).

<sup>8</sup> Lecher, *Ber.*, 53B, 577 (1920).

<sup>9</sup> Kharasch and Piccard, *THIS JOURNAL*, 42, 1855 (1920).

<sup>10</sup> DeWitt, *J. Am. Med. Assoc.*, 75, 1422 (1920).

<sup>11</sup> Schamberg, Kolmer, Raiziss and Trist, *J. Infectious Diseases*, 24, 547 (1919).

With these facts in mind, the authors entered upon the preparation and study of mercury derivatives of nitrophenol and its substitution products. In addition, they prepared mercury derivatives of various nitrosalicylic acids and derivatives of the same, for not only is salicylic acid itself a valuable germicide, but mercurated salicylic acid is regarded as an important factor in the treatment of syphilis.

In preparing compounds to be employed as chemotherapeutic agents, it is most desirable that they dissolve either in water, forming a neutral solution, or in just sufficient very dilute alkali to form a sodium salt. In addition, the resulting solution should be very stable. Solutions of sodium salts of organic mercury derivatives containing amino groups as a rule are unstable, the mercury splitting off from the molecule and depositing as a fine gray powder. Similar solutions of nitro compounds do not behave in this way. Alkaline solutions of the mercury derivatives of nitrophenol and nitrosalicylic acid can stand indefinitely without any mercury being deposited. Solutions of inorganic mercury salts and aromatic mercury derivatives in which the mercury is not very firmly attached, exhibit two marked characteristics. First, they precipitate the proteins in the blood, their therapeutic values thereby becoming diminished and secondly, surgical instruments immersed in them readily tarnish. Solutions of mercuraphen and other mercury nitro compounds possess these qualities only to a very slight extent.

The introduction of mercury into the nucleus is effected by warming the nitrophenol or salicylic acid in water for several hours with either mercuric acetate or oxide, usually resulting in the formation of a mixture of mono- and dimercurated products.

In the case of the acetate derivatives separation of the two compounds is very difficult since they are insoluble in the usual organic solvents except glacial acetic acid. Separation by the latter, however, is incomplete. An effective method is to transform the mixture into chloromercuri derivatives by means of hydrochloric acid and subject these to fractional crystallization from methyl or ethyl alcohol. In those instances where this method fails to produce satisfactory results, separation has been effected by fractional crystallization of the sodium salts from hot water. The greater part of the dimercury compound crystallizes out upon cooling. The filtrate containing all of the monomercury derivative and still some of the dimercury is then acidulated with hydrochloric acid producing the corresponding chloromercuri derivatives which precipitate. This mixture is then subjected to fractional crystallization from hot alcohol. The monomercury derivative is usually the more soluble and by repeated recrystallizations the dimercury compound is removed. Our experiences in the mercuration of *o*-nitrophenol are not in accordance with the results claimed by Hantsch and Auld.<sup>2</sup> By boiling together

an alcoholic solution of sodium *o*-nitrophenolate and an aqueous solution of one mol of mercuric acetate, they obtained a yellow precipitate to which they ascribed the following structural formula,  $O=C_6H_3 \begin{matrix} \diagup N \\ \diagdown H_g \end{matrix} \begin{matrix} \diagup O \\ \diagdown O \end{matrix}$ .

This product, they claimed, without any further purification, when analyzed, gave results for carbon and hydrogen remarkably close to the theoretical values.<sup>12</sup>

The product obtained by us was probably a mixture of the mono- and dimercury compounds from which it was impossible to separate either substance pure.

It is interesting to note that with 5-nitrosalicylic acid the dimercury derivative is obtained almost exclusively even though allowed to react with only equimolar quantities of mercuric oxide or acetate.

The mercury derivatives described in this paper belong to the series of the so-called half complex compounds in which one of the valences of the metal is attached to a nuclear carbon atom, the other to an hydroxyl, a halogen or other acid radical. The firmness of the linkage between the mercury and the nuclear carbon is not the same in the various half complex mercurials. In an earlier publication<sup>7</sup> one of the authors suggested an accurate method for estimating this firmness. None of the compounds described in this paper was affected by ammonium sulfide at room temperature within 30 minutes. At 80°, however, all yielded a precipitate of mercuric sulfide within the same time.

The positions of the mercury in our compounds have not been determined as yet. It is our intention to take up this question later in conjunction with other theoretical considerations. It is very possible, however, that the mercury assumes a position either *para* or *ortho* to an hydroxyl or a carboxyl group, since in several instances where the *para* and either one or both of the *ortho* positions are already occupied by a substituent, no substitution of the mercury in the ring occurred. Prolonged boiling of mercuric acetate with the following nitro compounds yielded no products of the type R-Hg.X: 2-iodo-4-nitrophenol, 2,4-dinitrophenol, 2-nitro-4-chlorophenol, 2,6-dibromo-4-nitrophenol and 2-nitro-4-chlorobenzoic acid.

### Experimental

**4-Acetoxymercuri-2-nitrophenol.**—A solution of 22.3 g. of mercuric acetate dissolved in 200 cc. of water with the aid of about 1 cc. of glacial acetic acid is added drop by drop to a warm solution of sodium *o*-nitrophenolate prepared from 10 g. of *o*-nitrophenol dissolved in 200 cc. of water and 10 cc. of 40% sodium hydroxide solution. An orange colored precipitate appears immediately. The whole is stirred mechanically for 2 hours, at the end of which time the precipitate acquires a yellow color. It is filtered

<sup>12</sup> Calc. for  $C_6H_3NO_3Hg$ : C, 21.36; H, 0.87. Found: C, 21.7; H, 0.85. Unfortunately, they give no results for mercury or nitrogen which according to their formula should be 56.34 and 4.15% respectively.

off and thoroughly washed with boiling water containing a slight amount of acetic acid. The crude product thus obtained is dissolved as completely as possible in 5% sodium hydroxide, filtered and reprecipitated by acetic acid. This precipitate is filtered off, washed with water, then methyl alcohol, and finally with ether until the last traces of nitrophenol are removed. The yield is 16.5 g. The product is easily soluble in hot glacial acetic acid and insoluble in the usual organic solvents.

Analyses for mercury and nitrogen indicate that the product is a mixture of the mono- and dimercury compounds. Four crystallizations from hot glacial acetic acid gave a product which apparently contained a larger proportion of the monomercury compound.

**4-Chloromercuri-2-nitrophenol.**—Our idea relative to the contamination of the corresponding acetate by the dimercuric acetate derivative is further substantiated in a study of the chloride. This is prepared from the previously described mixture of acetates by one of three methods: first, by suspending in water and transposing with 25% sodium chloride solution; second, by converting into the sodium salt by means of dil. sodium hydroxide solution, filtering off any insoluble residue and reprecipitating the filtrate by hydrochloric acid; third, by merely transposing the acetate with hydrochloric acid. In any case, the white product obtained is washed free from inorganic chlorides with water, taken up with methyl alcohol and boiled. Complete solution is not obtained. The insoluble residue is filtered off and repeatedly extracted with hot methyl alcohol. The substance remaining undissolved is dried *in vacuo* over sulfuric acid to constant weight. Mercury analyses indicate it to be a mixture of the mono- and dimercury compounds.

The original methyl alcoholic filtrate is allowed to crystallize. The product which deposits is recrystallized several times from methyl alcohol and dried to constant weight.

*Analyses.* Subs., 0.1983, 0.2006: HgS, 0.1384, 0.1374. Subs., 0.2000: N, 5.06 cc. of 0.1 N  $\text{H}_2\text{SO}_4$ . Calc. for  $\text{C}_6\text{H}_4\text{O}_2\text{NClHg}$ : Hg, 53.55; N, 3.75. Found: Hg, 53.18; 53.97; N, 3.57.

**Sodium hydroxymercuri-*o*-nitrophenolate (Mercurophen).**—This compound may be prepared from either the mercuric chloride or acetate derivative of *o*-nitrophenol by dissolving as completely as possible in dil. sodium hydroxide solution. Any insoluble residue is filtered off and the filtrate concentrated under reduced pressure. On cooling, a red solid crystallizes. This is thoroughly washed with ice-cold water and then recrystallized from hot water.

*Analyses.* Subs., 0.1998, 0.1998: HgS, 0.1218, 0.1230. Subs., 0.2000: N, 5.08 cc. of 0.1 N  $\text{H}_2\text{SO}_4$ . Calc. for  $\text{C}_6\text{H}_4\text{O}_2\text{NNaHg}$ : Hg, 53.05; N, 3.70. Found: Hg, 52.81; N, 3.58.

**2-Acetoxymercuri-4-nitrophenol.**—Aqueous solutions of equimolar quantities of sodium *p*-nitrophenolate and mercuric acetate are boiled for 2 hours. The resulting yellow precipitate is thoroughly washed with water, recrystallized thrice from hot glacial acetic acid and finally dried *in vacuo* over calcium chloride for 3 days when constant weight is obtained.

Analyses for mercury, nitrogen and carbon indicate that the product is a mixture of mono- and dimercury compounds.

**2-Chloromercuri-4-nitrophenol.**—The acetate mixture is converted into the mono-sodium salt by warming with dil. sodium hydroxide solution, filtering off any insoluble residue and allowing the filtrate to cool. An orange colored deposit is obtained, which is filtered off, dissolved in water and acidified with hydrochloric acid. A white precipitate of the chloride is obtained. This is recrystallized thrice from 50% ethyl alcohol.

*Analyses.* Subs., 0.1998, 0.1998: HgS, 0.1240, 0.1251. Subs., 0.2000: N, 5.26 cc.

of 0.1 *N* H<sub>2</sub>SO<sub>4</sub>. Calc. for C<sub>6</sub>H<sub>4</sub>O<sub>2</sub>NCIHg: Hg, 53.55; N, 3.75. Found: Hg, 53.50, 53.80; N, 3.71.

**4-Acetoxymercuri-2-nitroresorcin.**—Equimolar quantities of mercuric acetate and 2-nitroresorcin are heated on the water-bath for one-half hour. The orange colored precipitate obtained is filtered off, washed thoroughly with water, then ethyl alcohol, and finally with ether. It is dried *in vacuo* over calcium chloride for 48 hours. The yield is 75%. It is slightly soluble in water, ethyl alcohol, and ether.

*Analysis.* Subs., 0.2000: N, 4.8 cc. of 0.1 *N* H<sub>2</sub>SO<sub>4</sub>. Calc. for C<sub>8</sub>H<sub>7</sub>O<sub>6</sub>NHg: N, 3.38. Found: 3.38.

**4-Chloromercuri-2-nitroresorcin.**—By warming together 2-nitroresorcin suspended in water and freshly precipitated mercuric oxide on the water-bath for 2 hours, an orange colored precipitate is obtained. This is filtered off, washed with water, ethyl alcohol and ether and then converted into the chloride by 10% hydrochloric acid. The precipitate is washed free from inorganic chloride and dried.

It is a pale orange colored, amorphous powder, soluble in dil. sodium hydroxide solution, methyl and ethyl alcohols, ether, benzene and chloroform. It is extremely soluble in acetone and but slightly in hot water.

*Analyses.* Subs., 0.2000, 0.2000: HgS, 0.1195, 0.1193. Subs., 0.2000: N, 5.12 cc. of 0.1 *N* H<sub>2</sub>SO<sub>4</sub>. Calc. for C<sub>6</sub>H<sub>4</sub>O<sub>2</sub>NCIHg: Hg, 51.41; N, 3.59. Found: Hg, 51.50, 51.36; N, 3.61.

**5-Nitrosalicylic Acid.**—Unsatisfactory results were obtained upon attempting to prepare this acid by the methods described in the literature. By the method of Deninger,<sup>13</sup> the reaction proceeded rather violently and the final product consisted mostly of *o*-nitrophenol and 3,5-dinitrosalicylic acid. By the methods of R. Hirsch<sup>14</sup> and Hübner<sup>15</sup> the yields of pure acid as a rule were very small.

The following method which we adopted gave satisfactory results. 100 g. of salicylic acid was dissolved in 800 g. of glacial acetic acid. This was gradually nitrated by 50 g. of nitric acid (sp. gr. 1.50), the temperature being kept at 20° and the solution stirred mechanically. The mixture was allowed to stand at ordinary temperature until it assumed a dark red color, which requires from 30 to 45 minutes, and then was poured into 2000 g. of cracked ice. A yellow crystalline precipitate was produced almost immediately. After 1 hour it was filtered off and thoroughly washed with cold water.

To obtain the pure 5-nitrosalicylic acid, the crude product was suspended in 400 cc. of water, the whole heated just to boiling, filtered while hot and the filtrate discarded. The residue as a rule is the pure product, having a sharp melting point of 228°. In some cases the impurities are not quite all removed by the above procedure. By repeating with a smaller amount of water, the last traces of impurities are removed.

**3-Chloromercuri-5-nitrosalicylic acid.**—Upon heating 5-nitrosalicylic acid with a suspension of 2 mols of freshly prepared mercuric oxide in water at the boiling temperature for 12 hours, an orange colored substance is obtained. After filtering, thoroughly washing with water, alcohol, ether and subsequent drying in the desiccator, it showed upon analysis 67.85% mercury and 2.54% nitrogen. When warmed for a short time with hot alkali, part of the mercury is split off forming mercuric oxide which is removed by filtration and the filtrate allowed to cool. A slight amount of a white substance deposits. This is filtered off and the filtrate acidified with hydrochloric acid. A precipitate consisting of a mixture of the mono- and dimercury derivatives of 5-nitrosalicylic acid is thrown down at once. After these two compounds are thoroughly

<sup>13</sup> Deninger, *J. prakt. Chem.*, [2] 42, 550 (1890).

<sup>14</sup> Hirsch, *Ber.*, 33, 3239 (1900).

<sup>15</sup> Hübner, *Ann.*, 195, 45 (1879).



washed with water, separation is effected by boiling with 50% methyl alcohol, which dissolves the monomercury compound. The mixture is filtered hot and the monomercury compound crystallizes from the filtrate on cooling. It was recrystallized twice again from hot 50% methyl alcohol and dried.

*Analyses.* Subs., 0.0971: HgS, 0.0552. Subs., 0.2000: (Kjeldahl) 4.56 cc. of 0.1  $N$   $H_2SO_4$ . Subs., 0.1761:  $CO_2$ , 0.1214. Calc. for  $C_7H_4O_5NClHg$ : Hg, 47.96; N, 3.34; C, 20.09. Found: Hg, 47.83; N, 3.20; C, 19.38.

The fraction remaining undissolved in the hot 50% methyl alcohol is boiled with the same once more and recrystallized twice from 95% ethyl alcohol.

The product gave mercury analyses which indicated that it was a dimercury compound containing a considerable impurity of a trimercury compound.

3-Chloromercuri-5-nitrosalicylic acid is a pale yellow crystalline substance, slightly soluble in hot water, easily soluble in methyl and ethyl alcohols, ether and acetone. With dil. alkali a yellow solution is obtained. It melts with decomposition at  $235^\circ$ .

The dimercury derivative resembles in appearance the corresponding monomercury compound. It is insoluble in water, benzene and ether, but soluble in dilute alkali and hot ethyl alcohol. It melts with decomposition at  $238^\circ$ .

**Di-acetoxymercuri-5-nitrosalicylic acid.**—The product obtained by warming 5-nitrosalicylic acid with 2 mols of mercuric oxide is dissolved in boiling glacial acetic acid and filtered while hot. When the filtrate is cooled, a white crystalline precipitate is obtained which is recrystallized twice from boiling acetic acid. After drying *in vacuo* it assumes a pale yellow color and is insoluble in water, alcohol, ether and benzene; readily soluble in dil. sodium hydroxide solution.

*Analyses.* Calc. for  $C_9H_7O_7NHg$ : Hg, 45.35; N, 3.17; C, 24.49. Calc. for  $C_{11}H_9O_8NHg_2$ : Hg, 57.22; N, 2.00; C, 18.88. Found: Hg, 56.94; N, 2.91; C, 18.74.

This same substance can be prepared by boiling together 5-nitro-salicylic acid and aqueous solution of mercuric acetate.

An attempt was made to mercurize 3-bromo-5-nitrosalicylic acid<sup>16</sup> but the product was apparently a mixture of mono- and dimercury compounds.

**3,5-Dinitrosalicylic Acid.**—This acid was prepared according to the method of Hübner<sup>15</sup> with the following modification. Instead of purifying through the barium salt, we recrystallized from small amounts of hot water. The nitrogen analysis corresponded to the theoretical value and the melting point agreed with that found by Hübner.

Both mercuric acetate and freshly prepared mercuric oxide form mercury derivatives with 3,5-dinitrosalicylic acid which resemble each other both in appearance and physical properties. They are yellow crystalline substances, completely soluble in dil. alkali and insoluble in water, alcohol, ether, chloroform, benzene and acetone. They have no sharp melting points but begin to decompose at  $230^\circ$ . It was not found possible to obtain definite compounds from these products. They apparently consist of mixtures of mono- and dimercury compounds.

## Summary

1. The preparation and some of the chemical properties of the following compounds have been studied: 4-chloromercuri-2-nitrophenol, sodium hydroxymercuri-*o*-nitrophenolate (mercurophen), 2-chloromercuri-4-nitrophenol, 4-acetoxymercuri-2-nitroresorcin, 4-chloromercuri-2-nitroresorcin, 3-chloromercuri-5-nitrosalicylic acid, and di-acetoxymercuri-5-nitrosalicylic acid.

<sup>16</sup> Lellman and Grothmann, *Ber.*, 17, 2724 (1884).

2. The mercurization of 3-bromo-5-nitrosalicylic acid and of 3,5-dinitrosalicylic acid gave mixtures of mono- and dimercury compounds from which it was impossible to separate pure substances.

3. Modifications in the preparation of 5-nitrosalicylic acid and 3,5-dinitrosalicylic acid are described.

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[CONTRIBUTION FROM THE KENT CHEMICAL LABORATORY OF THE UNIVERSITY OF CHICAGO]

## A STUDY OF THE NITRO-ANILINES

BY MORRIS S. KHARASCH,<sup>1</sup> FREDERICK W. M. LOMMEN<sup>2</sup> AND ISADORE M. JACOBSON<sup>3</sup>

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The purpose of this investigation, as it developed, was twofold. It was desired, in the first place, to obtain additional information bearing upon the chemical constitution of the nitro-anilines and, second, to test the hypothesis advanced in a previous paper<sup>4</sup> as to the mechanism of mercurization of aromatic amines. It was pointed out in that paper that mercurization of aromatic amines proceeds probably in two stages: first, the addition of the mercury salt to the amino group forms an ammonium salt; this ammonium compound then rearranges, the most strongly positive group migrating to the *para* position or, that position being occupied, to the *ortho* position.

While this point of view seems to be generally applicable in the case of aromatic amines, it is quite conceivable that mercurization of amines capable of existing in the quinoid form, *e. g.*, the *ortho* and *para* nitro-anilines, might take place by the absorption of the mercury salt at the double bond.<sup>5</sup> Evidence of this type of substitution might well be obtained in the study of mercurization of the nitro-anilines and of the mono-nitro-diphenyl-amines. The present paper deals with the former phase of the problem.

As a general principle, one writes different structural formulas to indicate the tautomeric forms of a given compound. In the case of the *ortho* and *para* nitro-anilines, we might assume that, in solution, we are dealing with a mixture of the following tautomers in equilibrium,

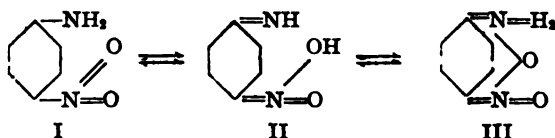
<sup>1</sup> National Research Fellow in Organic Chemistry.

<sup>2</sup> The material presented here is used by Frederick W. M. Lommen in his dissertation presented in partial fulfilment of the requirements for the degree of Doctor of Philosophy at the University of Chicago.

<sup>3</sup> Associate, Otho S. A. Sprague Memorial Institute, University of Chicago.

<sup>4</sup> Kharasch and Jacobsohn, *THIS JOURNAL*, **43**, 1894 (1921).

<sup>5</sup> The absorption of mercuric acetate by quinone, and also the behavior of the mercury salts of unsaturated aliphatic acids containing the double bond in the  $\alpha$ - $\beta$ ,  $\beta$ - $\gamma$  and  $\gamma$ - $\delta$  positions will be discussed in a subsequent paper by Kharasch.



the *para* compound being taken for illustration. In the case of *m*-nitro-aniline, however, structural formulas do not permit us to write such a simple quinoid arrangement. The question naturally arises whether our chemical reactions are compatible with the ordinary benzenoid structures for the 3 nitro-anilines, or whether the behavior of the *ortho* and *para* isomers is sufficiently different from that of the *meta* compound, and in agreement with a quinoid structure for those compounds.

It must be stated, however, that the present investigation is more of a qualitative nature and the real issue in question, as far as the present authors are concerned, is whether any of the tautomeric form II exists in solution. The presence of tautomer III in this solution should then follow, as in the case of sulfanilic acid, *p*-aminobenzoic acid, etc.

The only work of which the present writers are aware concerning the nitronic acid structures of the nitro-anilines is that of Baly and his collaborators on the absorption spectra of these compounds. In the first paper on the nitro-anilines, Baly, Edwards and Stewart<sup>6</sup> arrive at the conclusion that, since the nitro-anilines, in alcoholic solution, show the absorption bands present in quinones and diketones, while, in hydrochloric acid solution, they show none of these characteristics, the substances in alcoholic solution must have the quinoid form (II). This latter structure for the nitro-anilines has been criticized by Hantzsch,<sup>7</sup> since he claims that it is not applicable to the dialkyl nitro-anilines which also show similar absorption curves. Baly<sup>8</sup> in collaboration with Tuck and Marsden, in a subsequent paper, abandons the quinoid structures for the nitro-anilines and ascribes the absorption band to the "isorropesis between the nitro group and the aniline residue."

The main reason given by Baly for rejecting the quinoid structure for the nitro-anilines is as follows: "While it may be urged that the absorption of the free base and the monomethyl derivative (3-nitro-*p*-toluidine) is due to their existing in the quinoid form, it is difficult to see how the dimethyl compound can exist in this form, and yet the absorption spectra of all three are almost identical. The only difference is the shift toward the red accompanying the introduction of the methyl group." And, about the nitro-anilines, they say, "There is no difference at any moment between the free compounds and the dimethyl derivatives. The con-

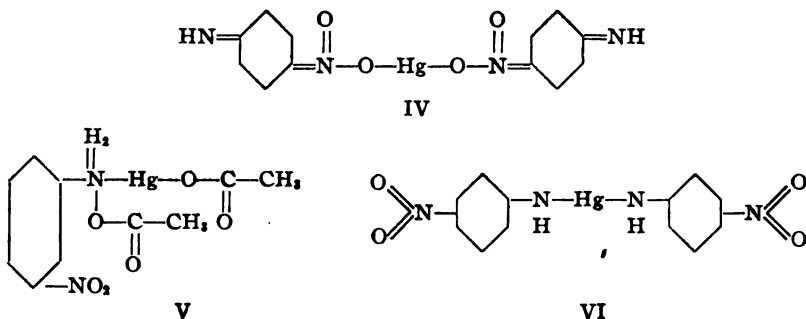
<sup>6</sup> Baly, Edwards and Stewart, *J. Chem. Soc.*, 89, 517 (1906).

<sup>7</sup> Hantzsch, *Ber.*, 43, 1668 (1910).

<sup>8</sup> Baly, Tuck and Marsden, *J. Chem. Soc.*, 97, 581 (1910).

clusion, therefore, is forced upon us that the same explanation of the color and absorption must be given in each. A simple quinoid compound is ruled out in the case of the dimethyl compound and hence we are compelled to abandon it in the case of the parent substances."

In spite of the later views advanced by Baly and the objections raised by Hantzsch to the nitronic acid structure for the *o*- and *p*-nitro-anilines, it may be profitable to examine the structure of the nitro-anilines in the light of the writers' work upon the mercury derivatives of these compounds. If the original view held by Baly as to the structure of the nitro-anilines in alcoholic solution were correct, then, in this solvent, the conditions would be most favorable for the formation of the tautomer II and, if a sufficiently insoluble salt of this tautomer could be produced by the addition of some base, it should precipitate. As a matter of fact, when an alcoholic solution of *o*- or *p*-nitro-aniline is treated with an aqueous solution of mercuric acetate, intensely colored compounds are precipitated in the course of a few seconds.<sup>9</sup> They behave as mercuric salts, reacting readily with ammonium sulfide in the cold to give a precipitate of mercuric sulfide. Their structures, from the viewpoint advanced would then be according to Formula IV, the *para* compound being taken for illustration. On the other hand, for the *meta* nitro-aniline, in which the formation of a quinoid compound of this type is not possible, the reaction with mercuric acetate is much slower, and the product, instead of being highly colored, as in the case of the *ortho* and *para* isomers, is almost white. Its analysis corresponds to Formula V, a different type of compound from that obtained from the *ortho* and *para* nitro-anilines.



It is interesting to note here that Jackson and Peakes<sup>10</sup> have obtained, in the case of *m*-nitro-aniline, as well as with its *ortho* and *para* isomers, a highly colored compound upon treating with nascent mercuric oxide. The analysis of the products, however, has led them to conclude that,

<sup>9</sup> The *ortho* and *para* isomers react, in this manner, not only with mercuric acetate, but in alcoholic solution they unite directly with mercuric oxide to give the same compounds.

<sup>10</sup> Jackson and Peakes, *Am. Chem. J.*, 39, 567 (1908).

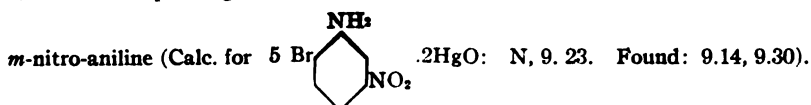
while the *o*-, *m*- and *p*-nitro-aniline salts probably have the structure shown in Formula VI, the *m*-nitro-aniline derivative must also contain a molecule of water of crystallization.

The formation of such a colored derivative in the case of *m*-nitro-aniline, using nascent mercuric oxide, and also of a *maroon* compound when an alcoholic solution of *o*-bromo-*m*-nitro-aniline (*i. e.*, a substituted *m*-nitro-aniline) is treated with an aqueous solution of mercuric acetate, as observed by the writers, is hardly compatible with the concepts developed above. Therefore, it became necessary either to reject the very tempting idea of quinoidation, as derived from the behavior of the *o*-, *p*- and *m*-nitro-anilines in alcohol solution with mercuric acetate, or to show that these *maroon* products obtained from *m*-nitro-aniline are chemically different from compounds capable of existing in the quinoid form, *e. g.*, *o*- and *p*-nitro-anilines, and substituted nitro-anilines such as nitro-toluidines, *p*-bromo-*o*-nitro-anilines, etc.

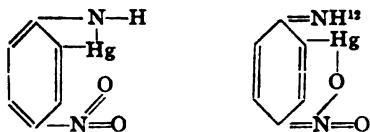
It is very significant in this connection that, while the colored compounds obtained from *o*- and *p*-nitro-anilines always give analyses which correspond to one mercury for two molecules of the nitro-aniline, those obtained from *m*-nitro-aniline and its bromo substitution products do not.<sup>11</sup> This suggests the possibility that the *m*-nitro-aniline and its derivatives yield addition compounds, while the *o*- and *p*-nitro-anilines yield true mercury salts of the nitronic acids. To test this deduction, the different colored compounds of the *o*-, *p*- and *m*-nitro-anilines were put into extraction thimbles in a Wiley extractor. Since neither ether nor benzene would wet the compounds satisfactorily, acetone was used as the extracting solvent. The deductions made were wholly verified since the acetone completely extracted the *m*-nitro-aniline and *p*-bromo-*m*-nitro-aniline from their respective colored mercury compounds, leaving in the thimble yellow mercuric oxide. The *o*- and *p*-nitro-aniline mercury salts, however, remained unchanged. This illustrates that there must also be a difference in the chemical formulas of these various colored compounds. Therefore, although the color of the *m*-nitro-aniline compounds with mercuric oxide resembles that of the *ortho* and *para* isomers, the facts advanced in support of quinoidation are not thus invalidated.

As further evidence of the nitronic acid structure for *o*- and *p*-nitro-anilines, the examination of the reactions of their mercurized products

<sup>11</sup> While the colored derivative of *m*-nitro-aniline gives analyses which correspond to two molecules of *m*-nitro-aniline to one molecule of mercuric oxide, the analysis of the reaction product obtained from *o*-bromo-*m*-nitro-aniline is more compatible with a formula corresponding to two molecules of mercuric oxide and five of the *o*-bromo-



toward alkalis and alkali carbonates is of considerable importance. Thus, when these derivatives, which are yellow, are treated with dil. alkali, red compounds are obtained whose analyses would correspond to either of the following structures,



VII

the derivatives obtained from *p*-nitro-aniline *ortho* mercuric chloride or acetate and sodium carbonate being taken for illustration.

However, if Formula VII were correct, one would expect that the compound would have undergone no color change. There are a few cases on record where we might suspect such an inner linkage between mercury and nitrogen as that expressed in Formula VII, but these compounds do not differ in color from the compound from which they are derived.<sup>13</sup>

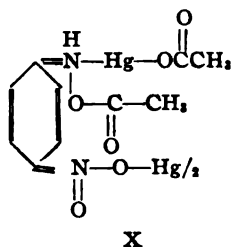
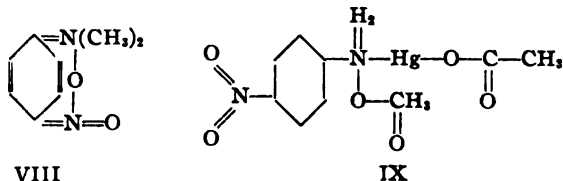
We find thus that the chemical behavior of the nitro-anilines suggests that in solution the *ortho* and *para* isomers might exist in the quinoid form. Of course, as with other tautomeric compounds, the solvent plays an important rôle in determining the amount of each of the tautomers present. For example, in alcoholic solution, tautomer II is favored, as indicated by the fact that the *o*- and *p*-nitro-anilines react quite readily with mercuric acetate to give quinone imide aci-nitro salts, while, in water solution, it is necessary to add alkali in order to obtain the same products. The objection raised by Baly to the nitronic acid structures for the *o*- and *p*-nitro-anilines may be overruled since it is possible to write the structures of the methylated nitro-anilines in the nitronic acid form. Thus, for *p*-nitro-dimethylaniline, we may write Formula VIII. A structure of this type is really more in accord with the chemical behavior than that usually written. Since it is an internal salt, we would not expect it to form salts with acids very readily. The only way in which the authors have been able to make the hydrochloride of this compound was by passing dry hydrogen chloride into its solution in anhydrous solvents. However, Hantzsch<sup>7</sup> has rejected the structure given above for *p*-nitro-dimethylaniline and thereby the theory of quinoidation in the case of the *o*- and *p*-nitro-anilines, on the basis that these compounds give absorption spectra similar to those obtained from the addition (?) compounds of polynitro benzols and aniline bases which cannot be formulated in that way. We do not believe that this objection invalidates

<sup>13</sup> This formula is quite comparable with that given by Hantzsch and Auld, *Ber.*, 39, 1115 (1906), for the aci-anhydrides of the mercurized nitrophenols.

<sup>13</sup> Pesci, *Gazz. chim. ital.*, 22, I, 373 (1892). Piccinini and Ruspaggiari, *ibid.*, 22, II, 609 (1892).

our conclusions as to the structures of the nitro-anilines. This matter will be discussed in greater detail in a subsequent paper.

The mechanism of mercurization of the nitro-anilines is, as yet, not definitely settled. There are at least three possible ways in which *o*- and *p*-nitro-anilines might be mercurized. In the first place, we might have the nitro-aniline molecule add on a molecule of mercuric acetate to form the ammonium salt (Formula IX).

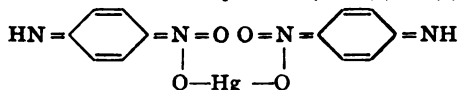


This would then rearrange, the mercury migrating to the *ortho* position. In favor of this supposition, we have the fact that the quinone-imide aci-nitro mercury salts of *o*- and *p*-nitro-anilines are not mercurized when heated with alcohol, while the addition of a little acetic acid effects the mercurization in a very short time, even in the cold.

The other possible mechanisms are the addition of mercuric acetate, in a similar manner to the above, but to the imido nitrogen of the mercury salt of the quinone-imide aci-nitronic salt, (Formula X). This compound then rearranges in the manner outlined above. Finally, we may also have direct absorption of the mercuric acetate by the double bond in the quinone-imide aci-nitro salt. As a guide in deciding the true mechanism of the mercurization of the nitro-anilines, the mercurization of mononitro-diphenylamines will be undertaken.

The positions taken by the mercury in the nitro-anilines is always *ortho* or *para* or *ortho-para* to the amino group.<sup>14</sup> This was established by preparing the acetyl derivatives of the various mercurized products, and subsequent replacement by bromine. The bromo derivatives were then compared with the respective synthetic products, prepared by other methods, and were found not to depress their melting points.

<sup>14</sup> It is of considerable interest, in this connection, that in the case of the dimercy compound of *m*-nitro-aniline the positions taken by the mercury are 2,4 ( $\text{NH}_2=1$ ,  $\text{NO}_2=3$ ) and not 4,6 as one might expect.

Experimental Part<sup>15</sup>*p*-Quinone-imide Aci-nitro Mercury Salt  $(C_6H_4(1)NH(4)NOO)_2.Hg$ 

This compound has already been prepared by Jackson and Peakes.<sup>10</sup> However, the following method of preparation has been found to be more practical than the one given by the above writers.

To a solution of 4.7 g. of *p*-nitro-aniline in 60 cc. of alcohol 4.6 g. of mercuric acetate dissolved in 8 cc. of water was added. Within the course of a few seconds a maroon precipitate was formed. This was collected on a filter, washed well with alcohol and ether and dried *in vacuo* over sulfuric acid to constant weight. Yield, 5.5 g.

*Analyses.* Subs., 0.2462: 25.6 cc. of dry  $N_2$  (23.5° and 745.4 mm.). Subs., 0.2204: Hg, 0.0923. Calc., for  $C_{12}H_{10}O_4N_2Hg$ : N, 11.82; Hg, 42.19. Found: N, 11.74; Hg, 41.88.

The compound is almost insoluble in cold water and the common organic solvents. However, when it is boiled with water or alcohol the filtrate is found to give a black precipitate when treated with ammonium sulfide, indicating that the mercury has not been substituted in the nucleus. It is decomposed immediately by acetic acid into mercuric acetate and *p*-nitro-aniline. When allowed to stand in alcohol, it remains for months without change. However, when a little acetic acid or mercuric acetate is added to the alcoholic suspension it is converted gradually in the cold, more rapidly in the hot, to a yellow compound described below. It decomposes at 300°.

*o*-Acetoxymercuri-*p*-nitro-aniline,  $[C_6H_3(1)NH_2(4)NO_2(2)HgO_2C_2H_5]$ .—This compound can be prepared by treating the above-mentioned salt with mercuric acetate or acetic acid. However, it was obtained in better yield by the following procedure. A solution of 9.2 g. of mercuric acetate in 15 cc. of water, to which a little acetic acid had been added, was mixed with a solution of 4.7 g. of *p*-nitro-aniline in 60 cc. of alcohol and the mixture was boiled for one hour. After this time the reaction was completed, as indicated by the fact that the filtrate gave no test for inorganic mercury when treated with ammonium sulfide. The reaction mixture was filtered hot. Upon cooling, the compound separated and was collected on a filter. It was recrystallized from hot alcohol to which a little acetic acid had been added. A beautiful yellow crystalline compound was thus obtained. This was washed with alcohol containing a few drops of acetic acid, and finally with ether. For analysis, the compound was dried *in vacuo* to constant weight.

*Analysis.* Subs., 0.2061: 12.80 cc. of dry  $N_2$  (20° and 721.7 mm.). Calc. for  $C_8H_5O_4N_2Hg$ : N, 7.08. Found: 6.89.

The compound is soluble in alcohol to which a few drops of acetic acid have been added. Upon treatment with solutions of sodium hydroxide or sodium carbonate, and even upon boiling with alcohol, the compound changes into a maroon substance which will be described in greater detail later in the paper. The compound turns red when heated, but does not melt below 300°.

*o*-Chloromercuri-*p*-nitro-aniline,  $[C_6H_3(1)NH_2(4)NO_2(2)HgCl]$ .—This compound may be obtained upon treating the alcoholic solution of the acetate, described above,

<sup>15</sup> Julius Rother, in his Inaugural Dissertation (Berlin, 1911) calls attention to a series of color changes which take place upon treating the nitro-anilines in alcoholic solution with mercuric acetate and to the stability of the various products to ammonium sulfide. Beyond that, however, no investigation was undertaken by him.



with an aqueous solution of sodium chloride or an alcoholic solution of calcium chloride. The yield is quantitative. For analysis, the compound was dried *in vacuo* to constant weight at 100°.

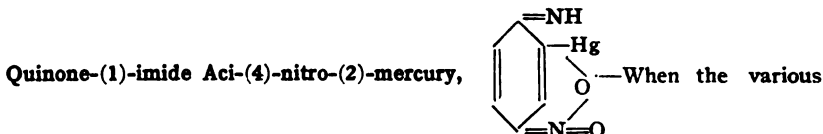
*Analysis.* Subs., 0.4440: AgCl, 0.1687. Calc. for  $C_6H_4N_2O_2HgCl$ : Cl, 9.50. Found: 9.37.

The compound is yellow. It is less soluble in alcohol than the acetate. It does not melt, even when heated to 300°. Like the corresponding acetate, it turns maroon when treated with sodium hydroxide.

*o,o'*-Di-acetoxymercuri-*p*-nitro-aniline,  $[C_6H_3(1)NH_2(4)NO_2(2,6)(HgO \cdot OC_2H_5)_2]$ .—When an alcoholic solution of 9 g. of *p*-nitro-aniline was boiled with an aqueous solution containing 18.4 g. of mercuric acetate, a disubstituted mercury derivative was obtained. To remove any of the monomercure compound which was formed the product was extracted with hot alcohol containing a little acetic acid. It was then dissolved in pyridine in order to remove a small amount of metallic mercury which had been formed in the reaction. The compound was then precipitated from this solvent by the addition of acetone. For analysis, it was dried *in vacuo* to constant weight.

*Analysis.* Subs., 0.2558: 10.40 cc. of dry  $N_2$  (22° and 738.3 mm.). Calc. for  $C_{16}H_{10}O_6N_2Hg_2$ : N, 4.28. Found: 4.57.

This compound is orange colored. It does not melt below 300°. When treated with sodium hydroxide or sodium carbonate solutions, and even upon boiling a suspension of the compound in alcohol, it changes into a red compound similar in structure to that described below.



mercury derivatives of *p*-nitro-aniline described above are heated or when they are treated with dilute solutions of sodium hydroxide or of sodium carbonate, and also when heated with alcohol, they are converted into maroon compounds. *o*-Acetoxymercuri-*p*-nitro-aniline furnishes a typical example of this reaction. This compound was dissolved in alcohol containing a little acetic acid, and upon treatment with an aqueous solution of sodium hydroxide, a maroon product was obtained in quantitative yield. For analysis, the compound was washed with alcohol and ether and dried *in vacuo* to constant weight.

*Analyses.* Subs., 0.2425: 18.30 cc. of dry  $N_2$  (24° and 728.9 mm.). Subs., 0.2305: Hg, 0.1362. Calc. for  $C_6H_4O_2N_2Hg$ : N, 8.34; Hg, 59.60. Found: N, 8.32; Hg, 59.09.

The compound is insoluble in all common organic solvents. When treated with acetic or hydrochloric acids, it turns yellow giving the acetate or chloride, respectively. It is stable to ammonium sulfide in the cold. It does not melt even when heated to 300°.

*o,o'*-Mercury-bis-*p*-nitro-aniline,  $[(C_6H_3(1)NH_2(4)NO_2)_2Hg]$ .—To prepare this compound, 1 g. of *o*-acetoxymercuri-*p*-nitro-aniline was moistened with alcohol and suspended in water. To this suspension an aqueous solution containing 3 g. of sodium thiosulfate was added. Within the course of a few minutes the compound was completely dissolved. The solution was then diluted with 20 cc. of water and the whole boiled for 6 minutes. A yellow precipitate soon formed. In order to test the completeness of the reaction a sample portion of the suspension was treated with sodium hydroxide solution. No color change was observed at the end of the period stated. However, should the color of the suspended solid change from yellow to orange or red, the reaction is incomplete and the solution should be boiled until no such test is obtained.

The compound was then extracted a few times with alcohol. Yield, 86%. For analysis the product was dried to constant weight *in vacuo*.

**Analyses.** Subs., 0.2798, 0.2055: 28.54 cc. of dry  $N_2$  (23° and 741.4 mm.), 20.80 cc. (23.5° and 746.5 mm.). Calc. for  $C_{12}H_{10}O_4N_4Hg$ : N, 11.76. Found: 11.52, 11.45.

The compound is greenish-yellow. It is insoluble in all common organic solvents. With sodium hydroxide it gives no color reaction, in distinction to unbridged compounds.

***o*-Acetoxymercuri-acetyl-*p*-nitro-aniline.**  $[C_6H_5(1)NH \cdot (CO \cdot CH_3)(4)NO_2(2)HgO \cdot OC_2H_5]$ .—To prepare this compound 4 g. of *o*-acetoxymercuri-*p*-nitro-aniline was boiled under a reflux condenser with 10 cc. of acetic anhydride and 30 cc. of ethyl acetate. After a short time the solid was completely dissolved. The solution was then filtered hot, and upon cooling a white crystalline product separated. This was collected on a filter and washed with alcohol. Yield, 50%. For analysis, the compound was dried *in vacuo* at 100° to constant weight.

**Analysis.** Subs., 0.2071: 12.10 cc. of dry  $N_2$  (21.5° and 731.8 mm.). Calc. for  $C_{16}H_{10}O_6N_2Hg$ : N, 6.40. Found: 6.53.

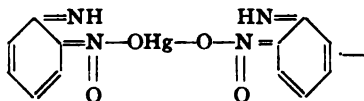
The compound is white and crystalline. It is soluble in ethyl acetate. With sodium hydroxide it gives no color change.

#### Determination of the Position of the Mercury in the Mercurized *p*-Nitro-aniline

The position of the mercury in the mono-mercury-substituted *p*-nitro-aniline was determined in the following manner. One mol of *o*-acetoxymercuri-acetyl-*p*-nitro-aniline was treated with 1 mol of potassium perbromide solution and the whole shaken until the color of the bromine had disappeared. The solid product of the reaction was collected on a filter and washed with water. It was then extracted with ether, the ethereal extract was evaporated to dryness, and the residue was recrystallized from hot water; m. p. 130°. When mixed with *p*-nitro-*o*-bromo-acetanilide prepared by synthetic methods, the melting point was not lowered. The position of the mercury is thus established as *ortho* to the amino group.

To determine the position of the mercury in the dimercury-substituted *p*-nitro-aniline the compound was first acetylated, in ethyl acetate suspension with acetic anhydride. The reaction was considered complete when the whole became almost white.<sup>16</sup> The acetylated compound thus obtained was treated with two mols of potassium perbromide in a manner similar to that used for the monomercury substituted derivative. A product was obtained which melted at 225–227°. When mixed with 4-nitro-2,6-dibromo-acetanilide the melting point was not lowered. The position of the mercury is thus established as being in the 2,6 positions ( $NH_2 = 1$ ).

**Quinone-(1)-imide Aci-(2)-nitro Mercury Salt,**<sup>17</sup>  $[(C_6H_4(1)NH(2)NO \cdot O)_2Hg]$



This compound was prepared from *o*-nitro-aniline by the same procedure as that used for the preparation of the corresponding *p*-nitro-aniline compound. The precipitation, however, was much slower than in the case of the latter compound. For analysis, the compound was washed with alcohol and ether, and dried *in vacuo* to constant weight.

<sup>16</sup> The compound thus obtained was insoluble in the common organic solvents and, owing to the presence of an appreciable quantity of metallic mercury formed in the course of the acetylation, was not analyzed.

<sup>17</sup> This compound has been prepared previously by Jackson and Peakes<sup>10</sup> using nascent mercuric oxide.



aniline derivative. The reaction in this case was found to take place much more slowly. For analysis the compound was dried *in vacuo* to constant weight.

**Analysis.** Subs., 0.2654: 13.8 cc. of dry  $N_2$  (22° and 737.0 mm.). Calc. for  $C_{12}H_{11}O_4N_2Hg$ : N, 5.84. Found: 5.87.

The compound is of a straw-yellow color. It is soluble in sodium hydroxide solution imparting to the solution a yellow coloration. M. p. 194° with decomposition.

***p*-Acetoxymercuri-acetyl-*o*-nitro-aniline**,  $[C_6H_3(1)N \cdot H \cdot CO \cdot CH_3](2)NO_2(4)HgO \cdot OC_2H_5]$ .—To prepare this compound, a water suspension of *p*-acetoxymercuri-diacetyl-*o*-nitro-aniline was treated with a dilute solution of sodium hydroxide. The compound dissolved, giving the solution a yellow color. The solution was then filtered immediately into dil. acetic acid. A yellow crystalline precipitate formed immediately. This was collected on a filter and washed with water and alcohol. For analysis the compound was dried *in vacuo* over sulfuric acid to constant weight.

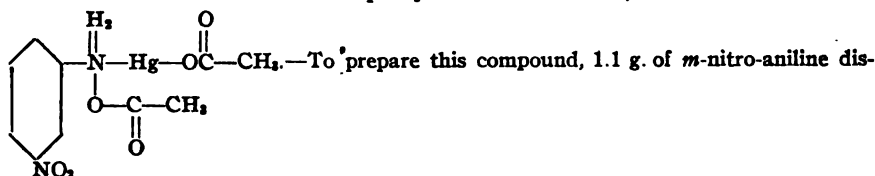
**Analysis.** Subs., 0.2835: 16.42 cc. of dry  $N_2$  (20° and 737.2 mm.). Calc. for  $C_{16}H_{10}O_6N_2Hg$ : N, 6.40. Found: 6.55.

The compound is yellow and crystalline. It dissolves in sodium hydroxide, forming a yellow solution. After a short time this solution yields a red precipitate, further de-acetylation having taken place. It melts with decomposition at 194°.

#### Determination of the Position of the Mercury in the Mercurized *o*-Nitro-aniline Derivative

To determine the position of the mercury in the mercury derivative, the diacetyl compound was treated with potassium perbromide in the same manner as already described for the corresponding *para* compound. A lemon colored compound was obtained which, when recrystallized from water, melts at 104°. When mixed with some known *o*-nitro-*p*-bromo-acetanilide the melting point was not lowered. The mercury is shown thus to be in the position *para* with respect to the amino group.

#### ***N*-*iso*-Mercuric-acetate-*m*-nitrophenylammonium Acetate,**



solved in 14 cc. of alcohol was added to a solution of 1.8 g. of mercuric acetate in 8 cc. of water. The solution soon acquired a dark color and considerable heat was evolved. After standing for 4 minutes a yellow solid separated and in a short time the entire mass became semi-solid. The compound was collected in a filter and washed well with acetone. For analysis it was dried *in vacuo* over sulfuric acid to constant weight.

**Analyses.** Subs., 0.2771, 0.3007: 14.00 cc. dry  $N_2$  (21° and 738.8 mm.), 15.40 cc. (25° and 717.0 mm.). Calc. for  $C_{10}H_{13}O_6N_2Hg$ : N, 6.12. Found: 5.70; 5.43.

The compound is slightly yellow. When treated with alcohol or water it decomposes to give a red substance. The filtrate when treated with ammonium sulfide gives a test for inorganic mercury.

***m*-Nitro-aniline-*p*-mercuric Acetate**,  $[C_6H_3(1)NH_2(3)NO_2(4)HgO \cdot OC_2H_5]$ .—To prepare this compound, 9.6 g. of mercuric acetate dissolved in 40 cc. of water was added to a solution of 4.2 g. of *m*-nitro-aniline in 60 cc. of alcohol. The solution soon changed into a pasty mass. Upon heating on the water-bath for 3 hours it gave no immediate test for

inorganic mercury with ammonium sulfide. The hot solution was then filtered and the solid residue extracted repeatedly with alcohol which contained a little acetic acid. A dark red residue remained which melted at 225°. This residue, which is the dimercurey-substitution product, will be described in more detail later in the paper. The first alcoholic extract was evaporated to dryness and the residue recrystallized from alcohol which contained a little acetic acid. For analysis the compound was dried *in vacuo* to constant weight.

*Analysis.* Subs., 0.1094: 7.00 cc. of dry N<sub>2</sub> (19° and 731.4 mm.). Calc. for C<sub>8</sub>H<sub>6</sub>O<sub>4</sub>N<sub>2</sub>Hg: N, 7.09. Found: 7.20.

The compound is yellow; m. p. 183°. A darkening of color is observed when it is treated with sodium hydroxide.

*o-p-Diacetoxymercuri-m-nitro-aniline*, [C<sub>6</sub>H<sub>3</sub>(1)NH<sub>2</sub>(3)NO<sub>2</sub>(4,2)(HgO·OC<sub>2</sub>H<sub>5</sub>)<sub>2</sub>].—This compound was prepared by boiling an alcoholic solution of 4.2 g. of *m*-nitro-aniline with 19.4 g. of mercuric acetate dissolved in water, until the solution gave no further test for inorganic mercury with ammonium sulfide. The precipitated compound was extracted repeatedly in order to remove any monomercurey substituted derivative which might have been present. For analysis the compound was dried *in vacuo* to constant weight.

*Analyses.* Subs., 0.6292: 25.36 cc. of dry N<sub>2</sub> (24° and 733.5 mm.). Subs., 0.2520: Hg, 0.1531. Calc. for C<sub>10</sub>H<sub>10</sub>O<sub>6</sub>N<sub>2</sub>Hg<sub>2</sub>: N, 4.28; Hg, 61.17. Found: N, 4.47; Hg, 60.76.

The compound is red; m. p. 225°. It is insoluble in the common organic solvents.

*p-Acetoxymercuri-acetyl-m-nitro-aniline*, [C<sub>6</sub>H<sub>3</sub>(1)NH·(COCH<sub>3</sub>)(3)NO<sub>2</sub>(4)HgO·OC<sub>2</sub>H<sub>5</sub>].—This compound was prepared from *p*-acetoxymercuri-*m*-nitro-aniline in the same manner as that described for the *p*-nitro-aniline derivative above. For analysis it was dried *in vacuo* over sulfuric acid to constant weight.

*Analysis.* Subs., 0.2522: 14.24 cc. of dry N<sub>2</sub> (18° and 739.5 mm.). Calc. for C<sub>10</sub>H<sub>10</sub>O<sub>6</sub>N<sub>2</sub>Hg: N, 6.40. Found: 6.45.

This compound is white. It melts with decomposition at 230°.

#### Determination of the Position of the Mercury in the Mercurized *m*-Nitro-aniline

The method of procedure used in determining the position of the *m*-nitro-aniline derivatives was similar to that used for the *para* compound. The compound obtained when recrystallized from water melted at 135–139°. When mixed with some known *p*-bromo-*m*-nitro-acetanilide the melting point was not lowered. The position of the mercury is thus shown to be *para* to the amino group.

To determine the position of the mercury in the dimercurey-substituted *m*-nitro-aniline, the latter compound was suspended in ethyl acetate and boiled under a reflux condenser with acetic anhydride until the whole became white.<sup>18</sup> The acetyl derivative thus prepared was treated with 2 mols of potassium perbromide, in the manner previously described. The product obtained was then filtered, dried and extracted with ether. The ethereal extract was evaporated to dryness, leaving a residue of melting point 141–146°. Upon recrystallization from 50% alcohol it melted at 150°. When mixed with known 2,4-dibromo-3-nitro-acetanilide the melting point was not lowered. The compound was then de-acetylated with conc. sulfuric acid at 120°. Upon dilution of this reaction mixture with water, a yellow product melting at 84–87° was obtained. Upon recrystallization from 50% alcohol, a product melting at 89° was obtained. When mixed with known 2,4-dibromo-3-nitro-aniline, the melting point was not lowered. This identifies the position of the mercury as being 2,4 with respect to the amino group (NO<sub>2</sub>=3).

<sup>18</sup> In the course of the reaction, an appreciable amount of metallic mercury was formed. Since the compound thus obtained is insoluble in the common organic solvents, it could not be purified, and therefore was not analyzed.

### Summary

1. The nitronic acid structure for the nitro-anilines is discussed. Evidence is given that is compatible with the assumption that, in alcoholic solution, the *o*- and *p*-nitro-anilines exist in two or more tautomeric forms. The fundamental difference between the mercury salts of the *o*- and *p*-nitro-anilines and that formed by the *meta* compound is pointed out.

2. The mercurization of the nitro-anilines is discussed.

3. The positions taken by the entering mercury in the nitro-anilines has been established as *ortho* or *para*, or *ortho-para*, to the amino group.

4. The preparation of the following compounds is described: *p*-quinone-imide-aci-nitro mercury salt, *o*-acetoxymercuri-*p*-nitro-aniline, *o*-chloromercuri-*p*-nitro-aniline, *o*-,*o'*-di-acetoxymercuri-*p*-nitro-aniline, quinone-(1)-imide-aci-(4)nitro-(2)-mercury, *o*-,*o'*-mercury-*bis-p*-nitro-aniline, *o*-acetoxymercuri-acetyl-*p*-nitro-aniline, quinone-(1)-imide-aci-(2)-nitro mercury salt, *p*-acetoxymercuri-*o*-nitro-aniline, *p*-chloro-mercuri-*o*-nitro-aniline, quinone-(1)-imide-aci-(2)nitro-(4)-mercury, *p*-acetoxymercuri-di-acetyl-*o*-nitro-aniline, *p*-acetoxymercuri-acetyl-*o*-nitro-aniline, *N*-*iso*-mer-curic acetate *m*-nitrophenylammonium acetate, *p*-acetoxymercuri-*m*-nitro-aniline, *o*, *p*-diacetoxymercuri-*m*-nitro-aniline, *p*-acetoxymercuri-acetyl-*m*-nitro-aniline.

CHICAGO, ILLINOIS

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

## ALIPHATIC ARSONIC AND ARSINIC ACIDS, AND ALIPHATIC-AROMATIC ARSINIC ACIDS<sup>1</sup>

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The extensive development of aromatic arsenicals as compared with those of the aliphatic series is in part explained by the fact that the most active and most effective trypanocidal drugs belong to the aromatic series. Another cause for the unbalanced development is found in the ease and convenience with which aromatic arsenicals can be synthesized. The methods of preparation for the arsenic compounds belonging to the aliphatic series are very numerous,<sup>2</sup> but they are quite unsatisfactory.

The arsonic ( $\text{RAsO}_3\text{H}_2$ ) and, to a less extent, the arsinic acids ( $\text{R}_2\text{AsO}_2\text{H}$ ) are substances from which many different types of compounds may be made, so that the lack of a satisfactory method of preparation of these has limited development in this field. The object of this research was to find an easy method for preparing these compounds and to apply such a method

<sup>1</sup> This communication is an abstract of a thesis submitted by A. J. Quick in partial fulfilment of the requirements for the degree of Doctor of Philosophy in Chemistry at the University of Illinois.

<sup>2</sup> See THIS JOURNAL, 28, 347 (1906) for a list of the known methods.

to the preparation of certain aliphatic-aromatic acids which might have therapeutic value.

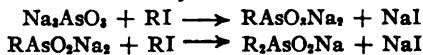
Of all methods available for preparing primary and secondary arsenic compounds, only one, namely the Meyer reaction, has any great importance. This consists in the treatment of sodium arsenite with an alkyl halide to give an arsonic acid, or the treatment of a sodium alkyl arsenite with an alkyl halide to give an arsinic acid.<sup>3</sup>

The reaction was first studied by G. Meyer<sup>4</sup> in 1883. Klinger and Kreutz<sup>5</sup> reinvestigated the reaction and developed it into a practical method for the preparation of sodium methyl arsonate. Auger<sup>6</sup> showed its application to the formation of dimethyl arsinic acid. Dehn<sup>7</sup> applied the method to the general synthesis of arsonic acids and obtained the salts of a number of the higher homologs in this way. It was necessary to use a rather uncertain and tedious procedure, however, for getting rid of the impurities and for the isolation of the product. Valeur and Delaby<sup>8</sup> reinvestigated the action of ethyl iodide on potassium arsenite, but added little to what was previously known so far as the isolation of the product was concerned.

The possibilities of the Meyer reaction were recognized to some extent in the preparation of toxic gases during the recent war. Ethyl dichloroarsine, which was used by Germany, was prepared by the action of ethyl chloride on sodium arsenite under pressure,<sup>9</sup> then subsequent reduction and treatment with hydrochloric acid. In this country methyl dichloroarsine was prepared by the action of dimethyl sulfate on sodium arsenite,<sup>10</sup> then subsequent reduction and treatment with hydrochloric acid. More recently methyl di-iodo-arsine<sup>11</sup> has been made in an analogous manner except that methyl iodide was used in place of dimethyl sulfate. In none of these cases, however, was the arsonic acid isolated.

The greatest disadvantage at present in the Meyer method for making arsonic acids lies in the difficulty with which the products are isolated. The method, as it has been used, consists in the treatment of an aqueous alcoholic solution of sodium arsenite with an alkyl iodide until titration

<sup>3</sup> It is probable that the alkyl halide reacts with the tautomeric forms of the sodium arsenite or sodium alkyl arsonite in each instance ( $\text{Na}_2\text{O}_2\text{AsNa}$  and  $\text{RNaO}_2\text{AsNa}$ ) thus producing compounds with the alkyl radical attached to arsenic.



<sup>4</sup> Meyer, *Ber.*, 16, 1440 (1883).

<sup>5</sup> Klinger and Kreutz, *Ann.*, 249, 147 (1903).

<sup>6</sup> Auger, *Compt. rend.*, 137, 925 (1903).

<sup>7</sup> Dehn, *Am. Chem. J.*, 35, 48 (1906); *THIS JOURNAL*, 28, 357 (1906).

<sup>8</sup> Valeur and Delaby, *Bull. soc. chim.*, 27, 370 (1920).

<sup>9</sup> *J. Ind. Eng. Chem.*, 11, 817 (1919).

<sup>10</sup> *Ibid.*, 11, 105 (1919).

<sup>11</sup> *J. Chem. Soc.*, 119, 426 (1921).

shows that most of the arsenite has reacted. When methyl iodide has been used the reaction mixture is merely allowed to cool and the sodium methylarsonate being insoluble in dilute alcohol, precipitates in practically pure state. The isolation of the higher homologs, however, is not so simple since the sodium salts are soluble in the dilute alcohol. In these latter cases, the method that has been employed is to distil the alcohol and any ether that is formed in the reaction, to acidify to incipient precipitation, then to oxidize the excess of sodium arsenite to sodium arsenate by means of chlorine and at the same time to precipitate free iodine, to filter the iodine, to precipitate the sodium arsenate in the cold with magnesia mixture, to filter this and finally precipitate the magnesium salt of the arsonic acid by boiling with an excess of magnesia mixture. The difficulties that must arise in obtaining a product in this way, especially one that is pure, can readily be seen. Moreover, Valeur and Delaby found that in the presence of aqueous alcoholic sodium arsenite, over 50% of the ethyl iodide is converted to ether, thus necessitating a large excess of the alkyl halide. The ether formation undoubtedly occurs in the preparation of arsonic acids of higher molecular weight.

In order to make the Meyer reaction applicable for wider synthetic work the objectionable features pointed out were eliminated. Alkyl bromides or chlorides were used instead of the iodides so that the free arsonic acids might be isolated directly by acidification; this is not possible when an iodide is used, since the liberated hydriodic acid formed immediately reduces the arsonic acid. The use of dilute alcohol as a solvent was given up and water alone was used, thus eliminating to a great extent the formation of ether. Heating and stirring were employed to hasten the reaction. The speed of the reaction was determined by titrating from time to time 1 or 2 cc. of the reaction mixture with standard iodine in order to show the amount of sodium arsenite unchanged. The isolation of the arsonic acid is then simple since it is merely necessary to concentrate the solution, filter off the sodium halide and acidify. The arsonic acid is precipitated in such form that, after one crystallization from alcohol or water, it is perfectly pure. With the higher, less soluble homologs the method is even simpler in that the arsonic acid may be precipitated directly without concentration from the reaction mixture, by means of hydrochloric acid.

There is no general method for the preparation of aliphatic arsinic acids. Sodium dimethyl arsinate is made commercially by the Cadet cacodyl reaction, but this reaction is limited to this substance and at best is beset with experimental difficulties. The condensation of an alkyl halide with arsenious chloride by means of sodium to produce dialkyl chloro-arsines which can be converted to the corresponding arsinic acids by bromination or chlorination and then hydrolysis, has been used as often as any other re-



action for making aliphatic arsinic acids. The method is unsatisfactory, however, owing to the fact that the pure dialkyl chloro-arsines are difficult to obtain and the conversion to arsonic acid does not give large yields. The Meyer reaction gives very good results. The arsonic acid made by the Meyer method is readily reduced with sulfur dioxide in the presence of hydrochloric acid to give good yields of the alkyl dichloro-arsine. This latter product is separated, then dissolved in 4 moles of sodium hydroxide and treated with an alkyl halide under the same conditions used in the preparation of arsonic acids. The reactions take place rapidly, only 4 hours or less being required in order to prepare any of the arsinic acids studied. The isolation of some of the arsinic acids, however, is a little more difficult than the isolation of the arsonic acids, on account of the great solubility in water of the lower homologs. It is necessary to neutralize the solution, then to concentrate and filter out the inorganic salts, and finally to acidify in order to precipitate the arsinic acid. If a salt of the arsinic acid is desired, the copper dialkyl arsinates are readily precipitated from a neutral solution by means of copper sulfate.

In studying the action of various alkyl bromides or chlorides on sodium arsenite or sodium alkyl arsenites, the activity of the halogen in the alkyl halide and the solubility of the alkyl halide are very important factors in determining the speed of reaction. Benzyl chloride, allyl bromide and ethylene chlorohydrin react very rapidly, whereas ethyl bromide or more particularly isopropyl bromide react slowly. The three halides just mentioned which react rapidly, give practically a complete conversion in  $\frac{1}{6}$  to  $\frac{1}{10}$  the time necessary with the simple alkyl halides. It is noticeable that with a series of alkyl halides the speed of reaction diminishes as the molecular weight of the alkyl halide is increased. Aryl halides cannot be used in this reaction. It was found also that phenoxy alkyl bromides or ethylene dibromide do not react with sodium arsenite under the conditions used.

The investigation on the arsinic and arsonic acids which has just been described was undertaken in connection with other researches, carried out with funds furnished by the Interdepartmental Social Hygiene Board, which had as their object the discovery of arsenic compounds of low toxicity and high trypanocidal action. All such active substances which have so far been discovered contain nitrogen. Moreover, this nitrogen has been in the form of an amino or substituted amino group in a benzene ring which holds the arsenic either in the form of an arsonic acid group or arseno group. A number of new arsenic compounds belonging to the class of aromatic-aliphatic arsinic acids have been prepared in some of which the nitrogen is substituted in the aliphatic group which is attached to the arsenic, and in others of which the nitrogen is both in the benzene ring holding the arsenic as well as in the aliphatic group. These substances may be represented by the compound formed between sodium phenyl arsenite and chloro-acetanilide.

$C_6H_5AsO_2Na_2 + ClCH_2CONHR \longrightarrow C_6H_5As(O_2Na)CH_2CONHR + NaCl$ . Compounds of this general structure are extremely easily produced by using practically the same conditions which are described for the preparation of the dialkyl arsinic acids. Because of the slight solubility in water of the reaction products, they are very readily isolated as the free acids. The reactions in practically every instance take place within a very few hours, and the yields are very nearly quantitative. The preliminary pharmacological results<sup>12</sup> show that these substances have a low toxicity, the lethal dose for rabbits varying from 250 to over 600 mg. per kg. of body weight. At the same time, however, the trypanocidal action is nil in some of the compounds, or low in most of the compounds, even though administered in relatively large amounts.

The reactions between sodium phenyl arsenite and various halogen compounds run just as smoothly as the sodium alkyl arsenites and much more readily than with the sodium arsenite. Whereas the phenoxyalkyl halides or ethylene dibromide do not react with sodium arsenite, they do react with the sodium alkyl or aryl arsenites to give the expected condensation products. The simple alkyl halides peculiarly, when condensed with sodium phenyl arsenite, give oily reaction products, although these substances when pure are crystalline solids.<sup>13</sup> A number of other condensations that were attempted yielded oily products and a method has not yet been developed by which these oils may be obtained as crystalline solids.

### Experimental

#### Synthesis of Arsonic Acids

**General Procedure.**<sup>14</sup>—One mole of arsenious oxide is dissolved in sufficient 10 *N* sodium hydroxide solution to produce tri-sodium arsenite. This is placed in a round-bottom flask fitted with an efficient mechanical stirrer and a reflux condenser. Slightly more than a mole of alkyl halide is added and the mixture stirred and refluxed until a cubic centimeter withdrawn from the reaction mixture and titrated with standard iodine shows that most of the sodium arsenite (80 to 90%) has reacted. The method of isolation is slightly different in each case and will be described under the individual compounds. In every case acidification with hydrochloric acid is involved. Excess acid must be avoided, as it tends to dissolve the arsonic acids.

**Sodium Methyl Arsonate,**<sup>15</sup>  $CH_3AsO_2Na_2$ .—The reaction between 99 g. of arsenious oxide, 300 cc. of 10 *N* sodium hydroxide solution and 150 g. of methyl iodide on warming

<sup>12</sup> Detailed pharmacological results will be published by Dr. A. S. Loevenhart of the University of Wisconsin when the investigation is completed.

<sup>13</sup> *Ber.*, **48**, 350 (1915).

<sup>14</sup> All analyses for arsenic were done by the method described by Robertson, *This Journal*, **43**, 182 (1921).

<sup>15</sup> *Ann.*, **249**, 147 (1903).

is complete in about 2 hours. An equal volume of alcohol is added to the mixture and the sodium methyl arsonate precipitates in very good yields. The product may be purified by dissolving in a small amount of water and reprecipitating with alcohol.

**Ethyl Arsonic Acid,  $C_2H_5AsO_3H_2$ .**—The reaction between 198 g. of arsenious oxide, 300 cc. of 10 *N* sodium hydroxide solution and 175 g. of ethyl bromide (110 g. is added at the beginning and 50 to 65 g. added gradually during the course of the reaction to compensate any loss due to volatilization), requires 24 to 48 hours before it is 90% complete. The reaction mixture is concentrated to a little less than half of its original volume and filtered to remove the sodium bromide which separates. The filtrate is now made neutral to phenolphthalein with hydrochloric acid, again concentrated to  $\frac{1}{2}$  or  $\frac{2}{3}$  its volume and filtered from sodium halide. It is next acidified with hydrochloric acid till congo red just commences to turn blue, once more concentrated to  $\frac{1}{2}$  or  $\frac{2}{3}$  its volume and filtered from sodium halide while still *hot*. On cooling, about 80 g. of needle-like crystals separates, together with a small quantity of sodium chloride. The filtrate will yield a larger quantity of ethyl arsonic acid if it is concentrated, filtered hot from the sodium halide and allowed to cool. This last treatment is repeated and from these two concentrations about 40 g. more of arsonic acid is obtained. The total yield of 120 g. is best purified from traces of salts by crystallizing from a small amount of water. The product then melts at 95–96° which is the same melting point as was found by La Coste.<sup>16</sup>

***n*-Propyl Arsonic Acid,  $C_3H_7AsO_3H_2$ .**—The reaction between 99 g. of arsenious oxide, 300 cc. of 10 *N* sodium hydroxide solution and 123 g. of *n*-propyl bromide requires 24 to 48 hours for 90% completion. The reaction mixture is treated exactly as with the ethyl arsonic acid. The propyl arsonic acid separates as small plates. As the acid is less soluble than the ethyl compound, it is obtained more readily and in better yields. The product is easily purified by recrystallization from a small amount of water and then has a melting point of 126–7° which agrees with that recorded in the literature.<sup>17</sup>

***n*-Butyl Arsonic Acid,  $C_4H_9AsO_3H_2$ .**—The reaction between 275 g. of *n*-butyl bromide, 198 g. of arsenious oxide and 600 cc. of 10 *N* sodium hydroxide solution requires 40 to 60 hours before 90% of the arsenious oxide has reacted. Small amounts of butyl bromide and butyl alcohol which have formed by hydrolysis are distilled and the solution is then neutralized to phenolphthalein with hydrochloric acid, concentrated to about half its volume and filtered. Upon adding hydrochloric acid till congo red just commences to turn blue, butyl arsonic acid separates as a thick crystalline paste. About 300 g. of the crude material is thus obtained. It is readily purified by a crystallization or two from hot water. It may also be recrystallized from alcohol. Butyl arsonic acid melts at 159–160° and in its general properties resembles the other arsonic acids. It forms an insoluble magnesium salt with magnesia mixture.

**Analyses.** Subs., 0.2000, 0.2000: required 21.2, 21.2 cc. of 0.1038 *N* I. Calc. for  $C_4H_9O_3As$ : As, 41.2. Found: 41.2, 41.2.

**Allyl Arsonic Acid,  $CH_2=CHCH_2AsO_3H_2$ .**<sup>18</sup>—The reaction between 250 g. of allyl bromide, 198 g. of arsenious oxide and 600 cc. of 10 *N* sodium hydroxide solution is 90% complete in 2 to 3 hours. The reaction mixture is neutralized to phenolphthalein with hydrochloric acid, concentrated to about  $\frac{1}{2}$  of its original volume and filtered. On acidifying the filtrate till congo red just commences to turn blue, the allyl arsonic

<sup>16</sup> La Coste, *Ann.*, 208, 34 (1881).

<sup>17</sup> THIS JOURNAL, 28, 352 (1906).

<sup>18</sup> During the preparation of this communication, an abstract of an English patent has appeared which describes the production of allyl arsonic acid and its salts. The procedure is somewhat different from the one used in this investigation. Brit. pat. 167,157; *Zentr.*, 1921, II, 1065.

acid precipitates in needle-like crystals, with a small amount of sodium chloride. The mixture is heated to boiling and filtered hot, thus removing most of the salt. The filtrate deposits crystals on cooling. These weigh 270 g., are pure after one recrystallization from water, and then melt at 128–9°.

*Analysis.* Subs., 0.2000: required 26.4 cc. of 0.09205 *N* I. Calc. for  $C_6H_5O_3As$ : As, 45.2. Found: 45.4.

**Benzyl Arsonic Acid,**<sup>19</sup>  $C_6H_5CH_2AsO_3H_2$ .—The reaction between 126 g. of benzyl chloride, 99 g. of arsenious oxide and 300 cc. of 10 *N* sodium hydroxide solution is more than 90% complete within 2 hours. An oily layer consisting of benzyl alcohol and a slight excess of benzyl chloride is always present at the end of the reaction. This is removed and the solution carefully neutralized to litmus with hydrochloric acid, then just a little more is added. On standing for about an hour, a small amount of flocculent material separates. This is filtered and the filtrate acidified till congo red commences to turn blue. Benzyl arsonic acid separates and is immediately filtered. It is washed with water and dried at 90°. The yields vary from about 130 to 135 g. After a crystallization from alcohol or water it melts at 167–8°.

**Attempts to Prepare Other Arsonic Acids.**—Ethylene chlorohydrin reacts very rapidly with sodium arsenite and in 10 minutes over 80% of the arsenious oxide has disappeared. The product, however, does not precipitate when treated in the way described for the alkyl arsonic acids. The solution is evaporated to an extremely small volume, the sodium halide filtered from time to time, and the residue is treated with absolute alcohol; practically all of the sodium halide separates and is filtered off. Upon evaporation of the filtrate an oil is obtained which is presumably the desired product, but as no method of purification was found it was not analyzed.

Similar results are obtained with trimethylene bromide, using two moles of sodium arsenite. The reaction takes place slowly. The product in this case is a thick oil which does not solidify.

Phenoxy-propyl bromide, phenoxy-ethyl bromide, *isopropyl* bromide and ethylene bromide react only very slowly with sodium arsenite and no products were isolated.

**General Procedure for Aliphatic Arsinic Acids.**—The conditions for the preparation of the arsinic acids are almost the same as those required for the preparation of arsonic acids. One mole of alkyl dichloro-arsine is dissolved in sufficient 10 *N* sodium hydroxide solution to produce the disodium alkyl arsenite. This is placed in a round-bottom flask fitted with an efficient mechanical stirrer and reflux condenser. Slightly more than a mole of alkyl halide is added and the mixture stirred and refluxed till titration shows that more than 90% of the disodium alkyl arsenite has reacted. Wherever the final products are only slightly soluble in water, direct acidification of the reaction mixture till congo red just commences to turn blue will cause the product to separate; where they are very soluble in water, it is necessary to proceed in a manner somewhat similar to that used for the isolation of the alkyl arsonic acids. Excess of acid causes the arsinic acids to become oily, so must be avoided.

**Diethyl Arsinic Acid,**<sup>20</sup>  $(C_2H_5)_2AsO_3H$ .—The reaction between 55 g. of ethyl bromide, 90 g. of ethyl dichloro-arsine and 210 cc. of 10 *N* sodium hydroxide requires from 4 to 6 hours before it is 90% complete. It is desirable to add 20 g. more of ethyl bromide

<sup>19</sup> THIS JOURNAL, 28, 347 (1906).

<sup>20</sup> *J. prakt. Chem.*, 63, 283 (1854).

toward the end of the reaction in order to replace that lost by volatilization. The excess of ethyl bromide is boiled away, the solution neutralized to phenolphthalein with hydrochloric acid, concentrated to half its volume and filtered from the salt which separates. The filtrate is acidified with hydrochloric acid till congo red just commences to turn blue, and concentrated once more to about  $\frac{2}{3}$  of its original volume when 50 g. of crude diethyl arsinic acid separate in plates. After two crystallizations from alcohol, the product is entirely free from a small amount of sodium chloride.

***n*-Butyl Dichloro-arsine,  $C_4H_9AsCl_2$ .**—A solution of 150 g. of crude *n*-butyl arsonic acid in 300 cc. of conc. hydrochloric acid is prepared. A few crystals of potassium iodide are added as a catalyst and then the solution is saturated with sulfur dioxide (about 2 hours is required). By this procedure, 100 g. of crude butyl dichloro-arsine separates. It is removed and the aqueous liquors are saturated with salt, thus yielding an additional quantity of the dichloride. The product is fractionated under diminished pressure and when pure consists of a colorless oil boiling at  $192-4^\circ$ .

**Analysis.** Subs., 0.5035:  $AgNO_3$ , 0.8426. Calc. for  $C_4H_9Cl_2As$ : Cl, 34.9. Found: 34.9.

***n*-Propyl *n*-Butyl Arsinic Acid,  $C_4H_9(C_3H_7)AsO_2H$ .**—The reaction between 25 g. of *n*-butyl dichloro-arsine, 60 cc. of 10 *N* sodium hydroxide solution and 20 g. of *n*-propyl bromide requires 3 to 5 hours for completion. The reaction mixture is made neutral to phenolphthalein with hydrochloric acid and then concentrated to half its volume. The salt which separates is filtered and the filtrate carefully acidified. The crystalline precipitate of arsinic acid is filtered and dried, and weighs 16 g. The filtrate is further concentrated to about  $\frac{2}{3}$  of its volume, filtered hot to remove the salt which separates, and then cooled to obtain a further amount of arsinic acid. The crude product must be crystallized once or twice from water to free it from sodium chloride, and then melts at  $127-8^\circ$ .

**Analyses.** Subs., 0.2000, 0.2000: required 21.1, 21.0 cc. of 0.09205 *N* I. Calc. for  $C_7H_{17}O_2As$ : As, 36.0. Found: 36.2, 36.1.

**Di-*n*-butyl Arsinic Acid,  $(C_4H_9)_2AsO_2H$ .**—The reaction between 61 g. of *n*-butyl bromide, 90 g. of butyl dichloro-arsine and 180 cc. of 10 *N* sodium hydroxide solution requires 3 hours for completion. The solution is neutralized, concentrated, and the salt filtered as described in the previous experiments. The filtrate is carefully acidified till congo red just commences to turn blue, and the crystalline dibutyl arsinic acid separates. After washing and drying it weighs 85 g. and after one crystallization from water it is perfectly pure and melts at  $137-8^\circ$ . Considerable care should be taken in acidifying the solution in order to precipitate the arsinic acid, since excess of acid causes the product to become oily.

**Analysis.** Subs., 0.2000: required 19.65 cc. of 0.09205 *N* I. Calc. for  $C_8H_{19}O_2As$ : As, 33.8. Found: 33.8.

The light-blue COPPER SALT,  $[(C_4H_9)_2AsO_2]_2Cu$ , is readily precipitated from a solution of dibutyl arsinic acid which has been just neutralized to phenolphthalein with sodium hydroxide by adding copper sulfate solution. The product is filtered, washed and dried for 2 hours at  $90^\circ$  in a vacuum. The yield is nearly quantitative.

**Analysis.** Subs., 0.2000: required 17.0 cc. of 0.09205 *N* I. Calc. for  $C_8H_{19}O_4As_2Cu$ : As, 29.6. Found: 29.2.

**General Procedure for Aliphatic-aromatic Arsinic Acids.**—One mole of the dichloro-arsine is dissolved in 4 moles of alkali in the usual way and 1 mole of the halogen compound added gradually, generally at room temperature. The reactions take place rapidly enough so that with the

sodium aromatic arsenites neither heating nor stirring are necessary in most cases to give excellent results. To isolate the products which for the most part are not very soluble in water, the reaction mixture is made neutral to phenolphthalein with hydrochloric acid. This causes the precipitation of a small amount of unchanged aromatic arsine oxide which is filtered. The filtrate is made acid with hydrochloric acid until congo red just commences to turn blue, to precipitate the product. If the product contains an amino group the final acidification must be done with care, not enough acid being added to redissolve the precipitate.

The majority of these compounds have decomposition points and not melting points. It was found that the decomposition points may vary considerably with the speed at which the temperature of the bath is raised.

**Phenylarsino Acetic Acid**,  $C_6H_5As(O_2H)CH_2CO_2H$ .—A mixture of 180 g. of phenyl dichloro-arsine and 365 cc. of 10 *N* sodium hydroxide solution is cooled and to this solution is added gradually with stirring 121 g. of sodium chloro-acetate in 150 cc. of water. An immediate reaction takes place and is complete within about 30 minutes, but it is best to allow the mixture to stand for 2 to 3 hours longer. The yield of product is 120 g. The substance may be purified by crystallization from hot water and then melts at  $141-2^\circ$  with decomposition.

*Analysis.* Subs., 0.2000: required 17.8 cc. of 0.09205 *N* I. Calc. for  $C_6H_5O_4As$ : As, 30.7. Found: 30.6.

**Phenyl Chloro-arsine Acetic Acid**,  $C_6H_5AsClCH_2CO_2H$ .—A solution is made of 60 g. of phenylarsino acetic acid in 180 cc. of conc. hydrochloric acid to which a few crystals of potassium iodide have been added. Sulfur dioxide is passed through to saturation and the phenyl chloro-arsine acetic acid separates in the form of plates. The yield is practically quantitative. The product is purified by crystallization from chloroform and then melts at  $102-3^\circ$ . Phosphorus pentachloride in chloroform solution converts the substance into phenyl dichloro-arsine.

*Analyses.* Subs., 0.2000: required 15.8 cc. of 0.09205 *N* I. Calc. for  $C_6H_5O_2ClAs$ : As, 30.4. Found: 30.7.

Subs., 0.5000:  $AgNO_3$ , 0.3430. Calc. for  $C_6H_5O_2ClAs$ : Cl, 14.4. Found: 14.3.

**Phenyl Bromo-arsine Acetic Acid**,  $C_6H_5AsBrCH_2CO_2H$ .—This is produced in a manner analogous to that for the chloro compound and after recrystallization from chloroform melts at  $113-4^\circ$ .

*Analysis.* Subs., 0.5000:  $AgNO_3$ , 0.2880. Calc. for  $C_6H_5O_2BrAs$ : Br, 27.5. Found: 27.1.

**Phenylarsino Acetanilide**,  $C_6H_5As(O_2H)CH_2CONHC_6H_5$ .—A solution of 35 g. of phenyl dichloro-arsine in 65 cc. of 10 *N* sodium hydroxide solution is made and with mechanical stirring 28 g. of chloro-acetanilide<sup>21</sup> is added. After 3 hours, when the reaction is complete, the solution is diluted with an equal volume of water before proceeding in the usual way. The product weighs 50 g. after washing with water and drying. It is purified by crystallization from water and then forms small needles melting at  $182-3^\circ$  with evolution of gas.

*Analysis.* Subs., 0.2000: required 12.2 cc. of 0.09205 *N* I. Calc. for  $C_{14}H_{14}O_2NAs$ : As, 23.5. Found: 23.7.

<sup>21</sup> THIS JOURNAL, 39, 1439 (1917).

**Phenyl Bromo-arsine Acetanilide**,  $C_6H_5AsBrCH_2CONHC_6H_5$ .—This product is made in a manner similar to that for phenyl bromo-arsine acetic acid, using 20 g. of phenylarsino acetanilide, 10 cc. of glacial acetic acid, 20 cc. of constant-boiling hydrobromic acid and 30 cc. of water containing a few crystals of potassium iodide. After saturation with sulfur dioxide, an oil separates which solidifies on standing. The compound is crystallized from methyl alcohol, and then melts at 108–110°.

*Analysis.* Subs., 0.4000:  $AgNO_3$ , 0.1900. Calc. for  $C_{14}H_{13}ONBrAs$ : Br, 21.9. Found: 22.4.

**Phenylarsino Acetphenetidine**,  $C_6H_5As(O_2H)CH_2CONHC_6H_4OC_2H_5(p)$ .—The reaction between 18 g. of chloro-acetphenetidine<sup>22</sup> and 19 g. of phenyl dichloro-arsine in 35 cc. of 10 *N* sodium hydroxide solution takes place and is complete in a few hours. The product crystallizes from alcohol in needles which melt at 175° with decomposition.

*Analysis.* Subs., 0.2000, 0.2000: required 10.70, 10.75 cc. of 0.1038 *N* I. Calc. for  $C_{16}H_{18}O_4NAs$ : As, 20.6. Found: 20.8, 20.9.

**Phenylarsino Aceto-arsanilic Acid**,  $C_6H_5As(O_2H)CH_2CONHC_6H_4AsO_3H_2(p)$ .—A solution of 31 g. of sodium chloro-acetoarsanilate<sup>23</sup> in 50 cc. of water is added gradually to 22 g. of phenyl dichloro-arsine in 45 cc. of 10 *N* sodium hydroxide solution. The reaction is complete in 2 hours. The chalky white material is extracted with a large amount of hot water, then with hot alcohol, and finally dried at 110°. As it is insoluble in water or the common organic solvents, it cannot be recrystallized. It may be dissolved in alkali, however, and reprecipitated by acidification. It does not melt below 250°.

*Analysis.* Subs., 0.2000, 0.2000: required 17.4, 17.4 cc. of 0.1038 *N* I. Calc. for  $C_{14}H_{15}O_5NAs_2$ : As, 33.8. Found: 33.8, 33.8.

**Phenylarsino *o*-Aceto-amino Benzoic Acid**,  $C_6H_5As(O_2H)CH_2CONHC_6H_4CO_2H(o)$ .—A solution of 22.5 g. of sodium *o*-chloro-aceto-amino benzoate<sup>24</sup> in 50 cc. of water is added to 22 g. of phenyl dichloro-arsine in 40 cc. of 10 *N* sodium hydroxide solution. The reaction takes only a short time for completion. (The sodium *o*-chloro-aceto-amino benzoate is prepared in a similar manner to the preparation of *p*-chloro-aceto-amino benzoic acid described below.) The product is purified by boiling the alkaline solution with animal charcoal, filtering and reprecipitating with hydrochloric acid. It melts at 198–200° with decomposition.

*Analysis.* Subs., 0.2000: required 11.9 cc. of 0.09205 *N* I. Calc. for  $C_{14}H_{13}O_5NAs$ : As, 20.6. Found: 20.4.

**$\beta$ -Phenoxy-ethyl Phenyl-arsinic Acid**,  $C_6H_5As(O_2H)CH_2CH_2OC_6H_5$ .—The reaction between 45 g. of  $\beta$ -phenoxy-ethyl bromide, 45 g. of phenyl dichloro-arsine and 80 cc. of 10 *N* sodium hydroxide solution requires 4 to 6 hours for completion. Heating and mechanical stirring are necessary to get good results. The small excess of unchanged halide is removed first before isolating the product. The substance separates as an oil which soon crystallizes. After recrystallization from water it melts at 122–3° and weighs about 20 g.

*Analysis.* Subs., 0.2000: required 14.3 cc. of 0.09205 *N* I. Calc. for  $C_{14}H_{15}O_3As$ : As, 24.5. Found: 24.6.

**Ethylene Diphenyl-diarsinic Acid**,  $C_2H_4(C_6H_5AsO_2H)_2$ .—The reaction between 32 g. of phenyl dichloro-arsine, 120 cc. of 10 *N* sodium hydroxide solution and 60 g. of ethyl-

<sup>22</sup> THIS JOURNAL, 41, 1453 (1919).

<sup>23</sup> *Ibid.*, 41, 1810 (1919).

<sup>24</sup> *Ber.*, 38, 1684 (1905).

ene bromide requires 4 to 8 hours for completion. Heating and mechanical stirring are necessary. The product separates as an oil. On dissolving in dil. ammonium hydroxide, filtering and again precipitating by careful acidification with hydrochloric acid, an oil is formed which gradually solidifies. The product may be recrystallized from hot water or alcohol and melts at 209–11°.

*Analysis.* Subs., 0.2000: required 21.7 cc. of 0.09205 *N* I. Calc. for  $C_{14}H_{10}O_4As_2$ : As, 37.7. Found: 37.3.

Subs., 0.2000: required 8.8 cc. of 0.135 *N* NaOH. Found: 8.4 cc.

*p*-Amino-phenyl Dichloro-arsine Hydrochloride,\*  $(p)Cl_2AsC_6H_4NH_2HCl$ .—This product is precipitated in practically quantitative yields when a stream of sulfur dioxide is passed into a solution of one part of arsanilic acid dissolved in 3 parts of conc. hydrochloric acid. A crystal or two of potassium iodide is added as a catalyst.

*p*-Amino-phenylarsino Acetanilide,  $(p)H_2NC_6H_4As(O_2H)CH_2CONHC_6H_5$ .—This substance is prepared in the usual way from 58 g. of *p*-amino-phenyl dichloro-arsine hydrochloride in 100 cc. of 10 *N* sodium hydroxide solution and 34 g. of chloro-acetanilide. The reaction is complete in about an hour but is allowed to stand for several hours. The product may be purified by crystallizing from either water or alcohol. It melts at 181–2° with decomposition.

*Analysis.* Subs., 0.2000: required 13 cc. of 0.09205 *N* I. Calc. for  $C_{14}H_{11}O_2N_2As$ : As, 22.4. Found: 22.4.

*p*-Aceto-amino-phenylarsino Acetanilide,  $(p)CH_2CONHC_6H_4As(O_2H)CH_2CONHC_6H_5$ .—This compound is made from the one just described by warming for 15 minutes after the initial reaction has taken place, with a slight excess of acetic anhydride. The compound which separates upon diluting with water is washed with dil. hydrochloric acid, then with water, and finally dried. It crystallizes from hot water in plates which melt at 205–6° with decomposition.

*Analyses.* Subs., 0.2000, 0.2000: required 11.65, 11.65 cc. of 0.09205 *N* I. Calc. for  $C_{16}H_{17}O_4N_2As$ : As, 19.9. Found: 20.0, 20.0.

*p*-Glycyl-aminophenylarsino Acetanilide,  $HO_2CCH_2NHC_6H_4As(O_2H)CH_2CONHC_6H_5$ .—This compound is prepared from *p*-amino-phenylarsino acetanilide by heating 10 g. in 30 cc. of 4% sodium hydroxide solution, with 7 g. of chloro-acetic acid. After refluxing for 3 to 4 hours and allowing to cool, an oil separates which solidifies on standing, or sometimes a solid separates directly. The compound after crystallization from methyl alcohol melts at 199° with decomposition.

*Analyses.* Subs., 0.2000, 0.2000: required 11.15, 11.2 cc. of 0.09205 *N* I. Calc. for  $C_{16}H_{15}O_4N_2As$ : As, 19.1. Found: 19.2, 19.2.

*p*-Amino-phenylarsino Acetphenetidine,  $(p)H_2NC_6H_4As(O_2H)CH_2CONHC_6H_4O-C_6H_5(p)$ .—The reaction between 21 g. of chloro-acetphenetidine and 29 g. of *p*-amino-phenyl dichloro-arsine hydrochloride in 50 cc. of 10 *N* sodium hydroxide solution is complete in 3 hours. The product is crystallized from alcohol, then melts at 211.5–212.5°.

*Analyses.* Subs., 0.2000, 0.2000: required 11.5, 11.5 cc. of 0.09205 *N* I. Calc. for  $C_{18}H_{19}O_4N_2As$ : As, 19.8. Found: 19.8, 19.8.

*p*-Aceto-amino-phenylarsino Acetphenetidine,  $(p)CH_2CONHC_6H_4(AsO_2H)-CH_2CONHC_6H_4OC_6H_5(p)$ .—The product is made from the one just described by using the directions given under *p*-aceto-amino-phenylarsino acetanilide. On crystallization from alcohol it melts at 214–215° with decomposition.

*Analyses.* Subs., 0.2000, 0.2000: required 10.3, 10.3 cc. of 0.09205 *N* I. Calc. for  $C_{18}H_{17}O_4N_2As$ : As, 17.8. Found: 17.7, 17.7.

\* *Ber.*, 43, 917 (1910).



*p*-Amino-phenylarsino Acetoarsanilic Acid,  $(p)H_2NC_6H_4As(O_2H)CH_2CONHC_6H_4AsO_2H_2(p)$ .—The reaction between 29 g. of chloro-aceto-arsanilic acid in 20 cc. of 10 *N* sodium hydroxide solution and sodium *p*-amino-phenyl arsenite made by dissolving 29 g. of *p*-amino-phenyl dichloro-arsine hydrochloride in 50 cc. of 10 *N* sodium hydroxide solution, is complete within 3 hours. The product is purified by crystallization from hot water. It does not melt below 350°.

*Analyses.* Subs., 0.2000, 0.2000: required 18.8, 18.9 cc. of 0.09205 *N* I. Calc. for  $C_{14}H_{16}O_4N_2As_2$ : As, 32.7. Found: 32.3, 32.5.

*p*-Aceto-amino-phenylarsino Aceto-arsanilic Acid,  $(p)CH_2CONHC_6H_4As(O_2H)CH_2CONHC_6H_4AsO_2H_2(p)$ .—This compound is made by the general procedure already described under the other aceto compounds. It forms in poor yields. It is purified by crystallization from hot water. It does not melt below 250°.

*Analyses.* Subs., 0.2000, 0.2000: required 17.3, 17.3 cc. of 0.09205 *N* I. Calc. for  $C_{16}H_{18}O_6N_2As_2$ : As, 30.0. Found: 29.7, 29.9.

*p*-Chloro-aceto-amino Benzoic Acid,  $(p)ClCH_2CONHC_6H_4CO_2H$ .—A suspension of 10 g. of *p*-amino benzoic acid in a mixture of 50 cc. of glacial acetic acid and 50 cc. of saturated sodium acetate solution is treated slowly, with vigorous stirring, with chloro-acetyl chloride. A white amorphous solid precipitates, is filtered, washed and dried. For subsequent work the crude material is satisfactory, but it may be purified by crystallization from alcohol and then has a melting point of 239°.

*Analysis.* Subs., 0.2000:  $AgNO_3$ , 0.1575. Calc. for  $C_8H_7O_2NCl$ : Cl, 16.61. Found: 16.5.

*p*-Amino-phenylarsino *p*-Aceto-amino Benzoic Acid,  $(p)H_2NC_6H_4As(O_2H)CH_2CONHC_6H_4CO_2H(p)$ .—This reaction between 42 g. of *p*-chloro-aceto-amino benzoic acid in 10 cc. of 10 *N* sodium hydroxide solution and 58 g. of *p*-amino-phenyl dichloro-arsine hydrochloride in 100 cc. of 10 *N* sodium hydroxide solution is complete in a few hours. It forms needles from hot water, melting at 217° with decomposition.

*Analysis.* Subs., 0.2000: required 11.4 cc. of 0.09205 *N* I. Calc. for  $C_{14}H_{16}O_4N_2As$ : As, 19.8. Found: 19.6.

### Summary

1. It has been shown that aliphatic arsonic acids, aliphatic arsinic acids and aliphatic-aromatic arsinic acids may be very readily prepared by the action of various halogen compounds upon an aqueous solution of sodium arsenite, sodium alkyl arsenite or sodium aryl arsenite.

2. This method has been applied to the preparation of several alkyl arsonic acids, as well as to allyl and benzyl arsonic acids; also to simple and mixed alkyl arsinic acids.

3. This method has also been applied to the preparation of many compounds of the general formula  $RAs(O_2H)CH_2CONHR'$  where R is a phenyl, *p*-amino-phenyl or *p*-aceto-amino-phenyl group and R' is a phenyl or substituted phenyl group. The compounds dissolve readily in aqueous alkalis, giving solutions which possess relatively low toxicity but at the same time only a slight trypanocidal action.

URBANA, ILLINOIS

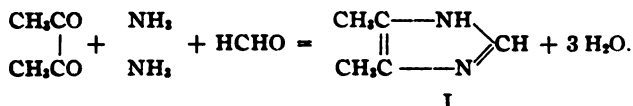
[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, YALE UNIVERSITY]

# THE UTILIZATION OF ETHYL GAMMA-DIETHOXY-ACETO-ACETATE FOR THE SYNTHESIS OF DERIVATIVES OF GLYOXALINE. AN ATTEMPT TO SYNTHESIZE HISTAMINE BY A NEW METHOD

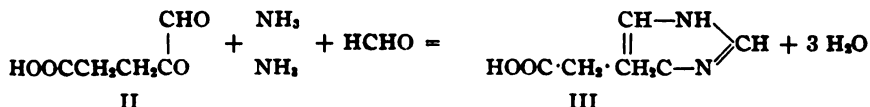
BY GEORGE W. PUCHER AND TREAT B. JOHNSON<sup>1</sup>

Received December 31, 1921

A fundamental reaction which has been applied successfully for the preparation of glyoxaline compounds is that involving the condensation of an *ortho*-diketonic compound with an aldehyde in the presence of ammonia. It was first utilized by Debus<sup>2</sup> for the synthesis of glyoxaline itself and the reaction has been used with success by several investigators since its discovery.<sup>3</sup> The interaction of diacetyl, for example, with ammonia and formaldehyde giving dimethylglyoxaline (I) is expressed by the following equation.



Windaus and Vogt<sup>4</sup> applied this type of reaction in one stage of their interesting synthesis of histidine and histamine, when they showed that the ketone-aldehyde (II) condenses normally with formaldehyde and ammonia with formation of  $\beta$ -imidazole-propionic acid (III), but outside



of this work no plan of synthesis, so far as the writers are aware, has been developed which involves the application of their principle for glyoxaline constructions of the type of histamine.

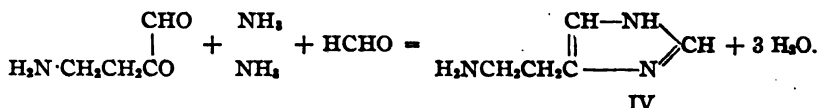
Analysis of the accepted structural formula of histamine (IV) reveals the fact that amino-ethyl-glyoxal,  $\text{H}_2\text{N} \cdot \text{CH}_2\text{CH}_2 \cdot \text{CO} \cdot \text{CHO}$ , is the *ortho*-ketone-aldehyde structure functioning in this cyclic molecule. In other words, this amine together with formaldehyde and ammonia theoretically have interacted in accordance with the principle outlined above giving a glyoxaline and the hypothetical synthesis of histamine (IV) may be expressed as follows.

<sup>1</sup> This paper is constructed from a dissertation presented by George Walter Pucher in June, 1920, to the Faculty of the Graduate School of Yale University in candidacy for the degree of Doctor of Philosophy. (T. B. J.)

<sup>2</sup> Debus, *Ann.*, **17**, 199 (1856).

<sup>3</sup> von Pechman, *Ber.*, **21**, 1417 (1888). Radziszewski, *ibid.*, **15**, 1493 (1882).

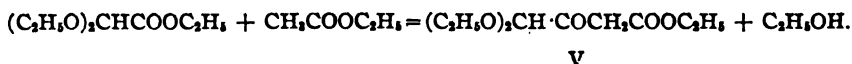
<sup>4</sup> Windaus and Vogt, *ibid.*, **40**, 3691 (1907).



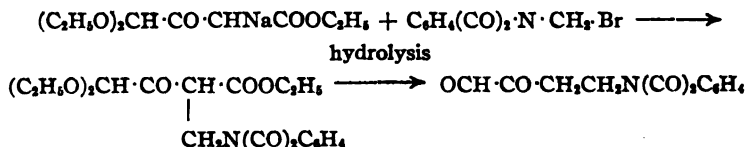
If we extend this series to the higher homologs it will be observed, for example, that the corresponding aminopropyl-glyoxal,  $\text{NH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{COCHO}$ , is the *ortho*-ketone-aldehyde which would be productive of the next higher homolog of histamine by condensation with ammonia and formaldehyde. In other words, a synthesis, which would permit of the formation of this series of glyoxal amines, theoretically would enable us to synthesize by a new method a series of glyoxaline bases related to histamine.

This analysis of the histamine molecule together with the fact that at present we have very scanty knowledge of aminoglyoxaline combinations of the above type created a renewed interest in the study of new methods of synthesis in this interesting biochemical field. Such a method of synthesis applicable to histamine alone would have many advantages over those that already have been applied. It would be a more direct method of approach and involve a smaller number of intermediate reactions.

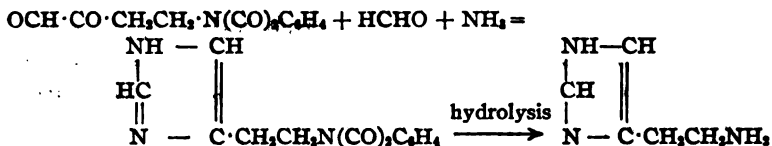
An organic reagent which is now available, but has never been utilized in the development of glyoxaline syntheses, is the very reactive  $\beta$ -ketone ester, namely, ethyl  $\gamma$ -diethoxy-aceto-acetate (V) which is obtained easily in a pure state by condensation of ethyl diethoxy-acetate<sup>5</sup> with ethyl acetate. Not only does it contain an acetal structure which is extremely susceptible to hydrolysis in acid solution, but it also contains a reactive methylene group which permits of the carrying out of fundamental reactions characteristic of a normal  $\beta$ -ketone ester.



The synthesis which we attempted to develop by use of this reagent is expressed in its different stages by the formulas given below and, as will be readily seen by inspection, its successful application depends primarily on a normal and smooth interaction between the sodium salt of the  $\beta$ -ketone ester and bromomethyl-phthalimide. So far as the writers



<sup>5</sup> Dakin and Dudley, *J. Chem. Soc.*, 105, 2453 (1914). Johnson and Cretcher, *THIS JOURNAL*, 37, 2144 (1915).



are aware, no one has even utilized this primary halide in an alkylation experiment, while it is well known that the higher homolog bromo-ethyl-phthalimide,  $\text{C}_6\text{H}_4(\text{CO})_2\text{NCH}_2\text{CH}_2\text{Br}$ , and bromopropyl-phthalimide,  $\text{C}_6\text{H}_4(\text{CO})_2\text{N} \cdot \text{CH}_2\text{CH}_2\text{CH}_2\text{Br}$ , react normally in such transformation. The phthalimido combinations were selected for this work for two reasons, first to offer protection to the amino group so as to avoid intramolecular condensation after formation of the alkylation product, and second to increase the molecular weight so as to insure the possibility of obtaining crystalline reaction products.

Thus far we have not been successful in bringing about the change representing the first stage of this new synthesis of histamine, namely, the interaction of bromomethyl-phthalimide with the ketone ester. The reaction has been applied under the normal conditions generally employed for reactions of this type, namely, by operating with the sodium salt of the ketone ester in alcohol solution, and also by alkylation of the sodium salt in anhydrous benzene, but with this ketone ester and also with ethyl aceto-acetate we obtained no evidence of the formation of alkylation products containing nitrogen.

Bromomethyl-phthalimide interacts with the sodium salts of these respective ketone esters with formation of sodium bromide, organic compounds which contain no nitrogen and *phthalimide*. Ethyl aceto-acetate is much more reactive towards this halide than is ethyl  $\gamma$ -diethoxy-aceto-acetate, but in both cases we were able to isolate over 80% of the calculated yield of phthalimide. In other words, bromomethyl-phthalimide interacts as though it had an entirely different constitution from that of a primary halide,  $\text{R} \cdot \text{CH}_2\text{Br}$ . While this halide reacts in a quite unexpected manner we find that its next higher homolog bromo-ethyl-phthalimide interacts smoothly with the  $\beta$ -ketone esters with the formation, respectively, of normal alkyl derivatives. We obtained no evidence in this case of the formation of phthalimide. A full description of these reactions and the characteristics of the products of reaction are given in the experimental part of this paper.<sup>6</sup>

The method of preparing bromomethyl-phthalimide has been greatly

<sup>6</sup> We are now engaged in the study of the mechanism of this quite abnormal reaction, but the work has been delayed much since the departure of Mr. Pucher from this laboratory. This research will involve not only a study of the action of these halogenated alkyl derivatives of phthalimide, but we shall also incorporate into our work an investigation of the action of halogenated ethers,  $\text{ClCH}_2 \cdot \text{O} \cdot \text{C} \cdot \text{H}_5$ , on ethyl  $\gamma$ -diethoxy-aceto-acetate. Very promising results have already been obtained by my colleague Professor A. J. Hill, who is extending the research into the pyrimidine series. (T. B. J.)

improved so that this reagent is now made available in any quantity desired. The compound has received hitherto very little attention, and in the experimental part are described several derivatives whose preparation illustrates its pronounced activity. This research will be continued in this laboratory.

### Experimental Part

**Phthalimide,  $C_6H_4(CO)_2NH$ .**—Dunlop<sup>7</sup> prepared this reagent by heating phthalic anhydride with urea. Herzog<sup>8</sup> later applied the same reaction and showed that these reagents interact nearly quantitatively at 135° and that the reaction is strongly exothermic. Noyes and Cass<sup>9</sup> showed that ammonium carbonate can be substituted successfully for urea in this preparation. The yield of phthalimide by both procedures is good, but it has been our experience that the method of operating as recommended by Kuhara<sup>10</sup> is just as satisfactory and convenient. All of the reagent used in our research was made according to this method. The process is as follows. One hundred g. of phthalic anhydride is placed in a liter flask which is connected with an ammonia generator through a wash-bottle containing a strong solution of sodium hydroxide and a series of drying tubes charged with granulated calcium oxide. The flask containing the anhydride is heated in an oil-bath to 140° and when the anhydride has melted a moderately rapid stream of ammonia gas is passed over the surface of the liquid. There is immediately a rapid absorption of gas, and the temperature of the bath is finally raised to 160° where it is held until the reaction, which lasts about 2 hours is complete. The phthalimide solidifies in the flask and is easily purified by crystallization from hot water.

#### Condensation of Phthalimide with Formaldehyde. The Formation of Hydroxymethyl-phthalimide, $C_6H_4(CO)_2N \cdot CH_2OH$

Sachs<sup>11</sup> states that this primary alcohol is formed when phthalimide (10 g.) is heated with 10% formaldehyde solution (25 cc.) in a sealed tube at 100° but no statement is made regarding the yield obtained. It was found by experiment that heating under pressure is unnecessary and that phthalimide is converted almost quantitatively (90–93%) into hydroxymethyl-phthalimide when digested under a reflux condenser with an excess of 10–15% formaldehyde solution. Cautious evaporation of the filtrate after the reaction is complete, as reported by Sachs, is not necessary as the hydroxymethyl-phthalimide is very insoluble in cold, dil. formaldehyde solution. The alcohol is obtained easily in pure condition in the following manner. The finely pulverized phthalimide obtained from 100 g. of phthalic anhydride is suspended in a solution of 80 cc. of 40% formaldehyde, 200 cc. of water is added, and this then heated under a reflux condenser at 103–108° for 4 hours. when practically all of the phthalimide will have dissolved and the reaction is practically complete. The hot solution is then filtered if necessary and allowed to cool when the hydroxymethyl-phthalimide crystallizes in beautiful, colorless glistening plates melting at 141–142°. It crystallizes from hot benzene and melts after purification from this solvent at 140° which is the melting point recorded by Sachs. The yield of alcohol is 90 g.

**Bromomethyl-phthalimide,  $C_6H_4(CO)_2N \cdot CH_2Br$ .**—This compound is easily prepared by the action of hydrobromic acid on hydroxymethyl-phthalimide. Gabriel<sup>12</sup>

<sup>7</sup> Dunlop, *Am. Chem. J.*, **18**, 332 (1896).

<sup>8</sup> Herzog, *Z. angew. Chem.*, **32**, 301 (1919).

<sup>9</sup> Noyes and Cass, *THIS JOURNAL*, **42**, 1282 (1920).

<sup>10</sup> Kuhara, *Am. Chem. J.*, **3**, 27 (1881).

<sup>11</sup> Sachs, *Ber.*, **31**, 3230 (1898).

<sup>12</sup> Gabriel, *ibid.*, **41**, 242 (1908).

used fuming hydrobromic acid to bring about the change, and it has been our experience that the alcohol reacts incompletely with a weaker acid. On the other hand, if sulfuric<sup>11</sup> acid is added along with hydrobromic acid the reactivity is greatly accelerated and the bromide is formed smoothly with a more dilute hydrobromic acid. Our method of preparing the halide is as follows. Eighty g. of hydroxymethyl-phthalimide is digested for 2 hours at 50–60° with 150 cc. of hydrobromic acid (48%) and 45 cc. of conc. sulfuric acid. The reaction proceeds smoothly and is productive of a thick magma of the bromide crystals, which are separated by filtration and washed first with water and finally with dil. aqueous ammonia to remove all acid present and then dried at 80°. The yield is about 75 g.; m. p. 146–147°. Recrystallization of the halide from acetone gives a product melting at 148° or at the same temperature as assigned by Sachs.<sup>11</sup>

*Analyses.* Calc. for  $C_8H_6O_2NBr$ : N, 5.83; Br, 33.3. Found: N, 5.97, 5.98; Br, 33.4.

When prepared according to the above method bromomethyl-phthalimide is obtained as a colorless crystalline powder which has a slightly irritating action on the eyes. It gradually decomposes on standing at ordinary temperature in moist air with the liberation of bromine and discoloration of the product. It is decomposed easily by water with formation of the corresponding alcohol. Bromine is given off when the compound is exposed to ultra-violet light and it also suffers decomposition when warmed with nitric acid. The bromide can be crystallized from hot glacial acetic acid, but long heating leads to its destruction with the liberation of bromine.

Sachs<sup>11</sup> prepared this halide by direct bromination of methyl-phthalimide,  $C_8H_6(CO)_2N \cdot CH_3$ , at 160°. While this method enables one to obtain the compound it is, however, an extremely tedious process and the yields are very unsatisfactory. Furthermore, the quality of the product is poor. An attempt was made to improve the method by introducing iron as a catalyst, but the bromination was not accomplished successfully under such conditions.

#### The Action of Ethyl Alcohol on Bromomethyl-phthalimide

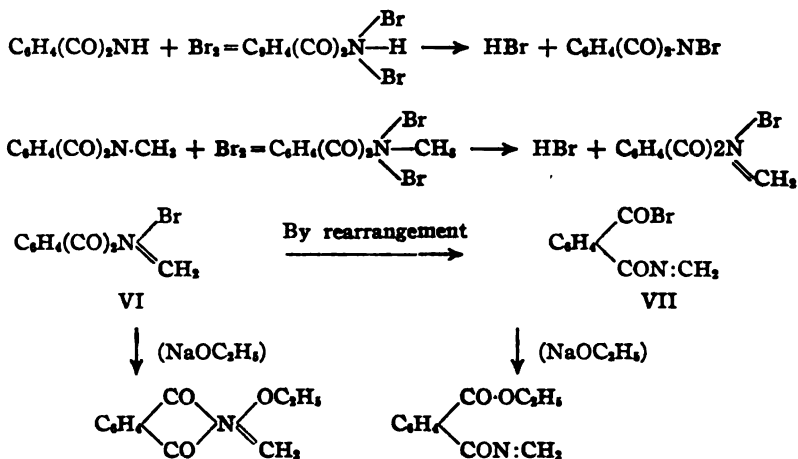
**Phthalimido Methylene Ether**,  $C_8H_6(CO)_2N \cdot CH_2 \cdot OC_2H_5$ .—Sachs<sup>11</sup> prepared this ether by the action of potassium cyanide or potassium iodide on bromomethyl-phthalimide in alcohol solution. The introduction of potassium salts is absolutely unnecessary here and the compound is formed smoothly by simply warming the bromide with alcohol. Two g. of the bromide was digested with 20 cc. of absolute alcohol for 3 hours. After evaporation of the solvent and recrystallization of the reaction product from acetone the ether was obtained in the form of long needles melting at 86°. This corresponds to the melting point assigned by Sachs. This same ether is also obtained by treatment of the bromide in alcohol solution at ordinary temperature with sodium ethylate. The change is not a quantitative one, however, and partial hydrolysis takes place leading to the formation of phthalic acid.

#### The Action of Chloromethylethyl Ether on the Potassium Salt of Phthalimide

**The Formation of Phthalimido Methylene Ether**,  $C_8H_6(CO)_2N \cdot CH_2OC_2H_5$ .—In the bromination of methyl-phthalimide Sachs<sup>11</sup> represents the substitution of halogen as taking place in the methyl group giving a primary halide,  $C_8H_6(CO)_2N \cdot CH_2Br$ . The possibility that an isomeric compound of entirely different structure might be formed here was not considered by him. If one assumes that both phthalimide and its methyl derivative interact with bromine in an analogous manner, namely, by addition of halogen to nitrogen with formation primarily of pentavalent compounds, it is conceivable that this monobromo derivative of methyl-phthalimide may have an entirely

<sup>11</sup> Kamm and Adams, *THIS JOURNAL*, 42, 299 (1920).

different constitution from that assigned to it by Sachs and Gabriel. Theoretically, the addition product might dissociate with formation of an unsaturated derivative such as is represented below in Formula VI. If such a combination, or its rearrangement product (Formula VII), is formed the constitution would not be revealed necessarily by reaction with sodium ethylate. The interaction might be expected to lead to the formation of an ethoxy derivative having an entirely different constitution from that assigned to the ethyl ether described above, but such data should be accepted with caution as it has already been shown that phthalimido derivatives<sup>14</sup> are very susceptible to isomeric change in the presence of sodium ethylate and also that intramolecular rearrangements can be brought about easily in organic combinations containing the grouping  $-N=CH_2$ .<sup>15</sup>



In the light of these considerations it was important, therefore, to establish the structure of the ethyl ether by direct synthesis. This is easily accomplished by allowing the potassium salt of phthalimide to react with chloromethylethyl ether  $\text{ClCH}_2\text{OC}_2\text{H}_5$ . Fifteen g. of the potassium salt and 10 g. of the chloro ether dissolved in 50 cc. of dry benzene were digested on a steam-bath for 5 hours. The potassium salt slowly disappeared and potassium chloride separated. On evaporating the solvent the ethyl ether was obtained in the form of an oil which solidified immediately on cooling. After recrystallization from alcohol it melted sharply at  $86^\circ$ , and proved to be identical with the ether described above. The yield was practically that calculated.

**Phthalimidomethyl Thiocyanate,  $\text{C}_6\text{H}_4(\text{CO})_2\text{N}\cdot\text{CH}_2\cdot\text{SCN}$ .**—The fact that bromomethyl-phthalimide reacts like an acid halide and is easily decomposed by warming with alcohol with formation of hydrobromic acid suggested that it would interact also with potassium thiocyanate to form an isothiocyanate or a mustard oil. We now find that the reaction proceeds in the reverse order and is productive of a rhodanide or normal thiocyanate. This compound is obtained easily by interaction of potassium thiocyanate with bromomethyl-phthalimide in acetone. Alcohol cannot be used as a solvent on account of its reactivity towards the bromide. Ten g. of the bromide was dissolved in 50 cc. of dry acetone and 4 g. of potassium thiocyanate added to the solution. There was an immediate reaction with precipitation of potassium bromide. After heating for 2 hours on a water-bath and then filtering hot to separate undissolved potassium

<sup>14</sup> Gabriel and Colman, *Ber.*, 33, 981 (1900).

<sup>15</sup> Unpublished data (T. B. J.).

bromide and potassium thiocyanate the acetone solution was concentrated by evaporation and finally cooled when the thiocyanate separated in the form of glistening plates. These were separated by filtration and the compound recrystallized from acetone when it melted at 147–148°. The substance gave a strong test for sulfur.

*Analyses.* Calc. for  $C_{10}H_6O_2N_2S$ : N, 12.85. Found: 12.85, 12.6.

This new thiocyanate crystallizes from acetone in yellow plates and its vapor is extremely irritating to the eyes, causing a burning sensation and inflammation of the eyeballs. That the compound has not the structure of an isothiocyanate is shown by its failure to react with aniline or ammonia to form thio-urea combinations. The compound is also not desulfurized by action of aqueous lead acetate.

#### The Action of Potassium Cyanide on Bromomethyl-phthalimide in Acetone Solution

Sachs investigated the action of potassium cyanide on this halide and applied the reaction in alcohol solution without success. Instead of obtaining the corresponding nitrile the ethyl ether was formed by interaction of the bromide with alcohol. In order to avoid this action of alcohol we applied the reaction with potassium cyanide in acetone, but here again, to our surprise, we obtained only abnormal results. For example, a mixture of 5 g. of bromomethyl-phthalimide and 2 g. of finely pulverized potassium cyanide was added to 25 cc. of acetone; the mixture was digested for 8 hours on a steam-bath and finally allowed to cool. The insoluble material was then separated by filtration and triturated with cold water to remove inorganic salts when 1.5 g. of a crystalline organic product was obtained which proved to be phthalimide. More of this same reagent was found in the acetone filtrate and when crystallized from alcohol melted at 228–230°. We obtained no evidence of the formation of a nitrile. Exactly the same result was obtained when potassium iodide was incorporated with potassium cyanide as a catalyst.

*Analyses.* Calc. for  $C_8H_4O_2N$ : N, 9.52. Found: 9.60, 9.4.

**Iodomethylphthalimide,  $C_8H_4(CO)_2N \cdot CH_2I$ .**—Gabriel states<sup>12</sup> that this iodide can be prepared by dissolving the corresponding alcohol in strong hydriodic acid. Sachs<sup>11</sup> failed to obtain the compound by allowing potassium iodide to act on bromomethyl-phthalimide in alcohol, the corresponding ether being formed instead. This latter reaction can be brought about successfully when acetone is used as a solvent in place of alcohol. Ten g. of the bromide and 7 g. of potassium iodide interacted in acetone solution completely after warming on the steam-bath for 2 hours. On concentrating the acetone solution and cooling, the iodide separated in a crystalline condition and after crystallization from ethyl acetate melted at 150°. This halide is a colorless crystalline substance which slowly decomposes at ordinary temperature and assumes a dark brown color due to separation of iodine. It is decomposed immediately by action of nitric acid at ordinary temperature with liberation of iodine.

*Analysis.* Calc. for  $C_8H_4O_2NI$ : N, 4.9. Found: 5.1.

Potassium cyanate and potassium nitrite failed to react with bromomethyl-phthalimide when heated with the latter reagent in acetone solution.

#### The Action of Bromomethyl-phthalimide on the Sodium Salt of Ethyl Aceto-acetate

In our preliminary study of this reaction we always operated with units of 11 g. of the  $\beta$ -ketone ester and 20 g. of the bromide. The reaction was also applied several times but for purposes of description the results of only one experiment will be recorded in detail. The method of operating was as follows. Two g. of sodium was dissolved in 70 cc. of absolute ethyl alcohol and the sodium salt of ethyl aceto-acetate prepared in the usual manner by dissolving 11 g. of the ketone ester in this alkaline solution. The alcohol solution of the sodium salt was then cooled to room temperature, 20 g. of finely



pulverized bromomethyl-phthalimide added to this at once, and the flask immersed immediately in ice water. There was an immediate reaction with evolution of heat and the bromomethyl-phthalimide gradually dissolved. Within a short time the alcohol acquired a turbid appearance and a crystalline precipitate began to deposit. The temperature of the solution did not rise above 60° throughout the operation and on standing the reaction was easily brought to completion, giving a solution perfectly neutral to litmus. The intensity and velocity of this reaction are revealed by reference to Table I.

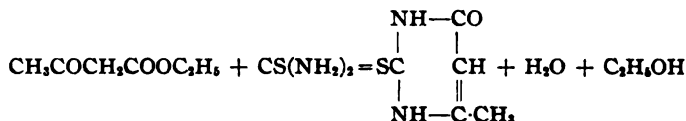
TABLE I

Time of reaction Min.	Temperature °C.	Time of reaction Min.	Temperature °C.
Start	23	7	48
2	44	11	45
3	50	36	23
5	59		

When the reaction was complete the solid material was separated by filtration and after drying at 100° weighed 18 g. On triturating this with cold water we extracted 6 g. of sodium bromide while the calculated amount possible from the reaction would be 8.2 g. The colorless crystalline material insoluble in cold water (12 g.) was apparently a pure substance and was identified as phthalimide melting at 228–230°. The calculated yield of the imide would be 16 g.

*Analysis.* Calc. for  $C_8H_5O_2N$ : N, 9.53. Found: 9.4.

The alcohol filtrate above was heated under diminished pressure at 100° to remove all excess of ethyl alcohol when a dark colored oil was obtained which deposited on cooling more sodium bromide and phthalimide. About 1 g. of the imide was recovered in this manner bringing the total yield to 13 g. or 81.3% of the calculated amount. This oil was triturated with water to remove sodium bromide and finally extracted with ether. After drying and evaporation of the ether we obtained 10 g. of a dark viscous oil which gave only a slight coloration with ferric chloride solution, and could not be heated to its distillation temperature under diminished pressure without decomposition. That the oil did not contain an appreciable amount of unaltered ethyl aceto-acetate was evidenced by the fact that no trace of 2-thio-4-methyluracil was formed by digestion of a fraction of the oil with thio-urea and sodium ethylate in absolute alcohol.<sup>18</sup> This oil is apparently



a mixture of at least two products one of which is soluble in cold aqueous alkali and the other insoluble. All attempts to obtain a definite, constant-boiling product by distillation under diminished pressure were unsuccessful on account of decomposition below the temperature of distillation.

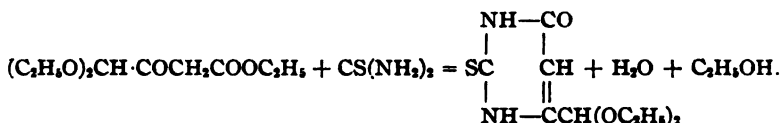
**Application of the Reaction in Benzene.**—Using exactly the same proportions of sodium, and ethyl aceto-acetate as described in the preceding experiment, the sodium salt of the ketone ester was prepared by interaction of these reagents in boiling benzene. When the formation of salt was complete the bromide (20 g.) was added and the reaction brought to completion by heating on the water-bath for 6 hours. The insoluble material was identified as a mixture of sodium bromide and phthalimide and the latter was obtained in practically the same amount as when the reaction was applied in alcohol

<sup>18</sup> Johnson and Heyl, *Am. Chem. J.*, 37, 628 (1907).

solution. It melted at 228–230°. On evaporating the benzene an oil was obtained which exhibited the same behavior as the oil obtained in the previous experiment. It could not be distilled under diminished pressure without decomposition.

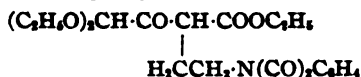
**The Action of Bromomethyl-phthalimide on the Sodium Salt of Ethyl  $\gamma$ -Diethoxy-aceto-acetate,  $(C_2H_5O)_2CHCOCH_2COOC_2H_5$**

The following proportions were used in this experiment: 2 g. of sodium, 70 cc. of absolute ethyl alcohol and 19 g. of the  $\beta$ -ketone ester. The reaction was carried out under exactly the same conditions as when ethyl aceto-acetate was used but it was our experience that the change was much less vigorous. In fact, in order to bring the reaction to completion it was necessary to heat on the steam-bath for about 3 hours before the alcohol became neutral to litmus. The reaction product was worked up in the same manner as before and about 80% of the calculated amount of phthalimide isolated. In addition a viscous oil was obtained which decomposed when an attempt was made to purify it by distillation under diminished pressure. A fraction of 5 g. of this oil was digested with thio-urea and sodium ethylate in alcohol solution, but we obtained no evidence of the formation of a pyrimidine compound as would be expected if any unaltered  $\beta$ -ketone ester were present.



**The Action of Bromo-ethyl-phthalimide on the Sodium Salt of Ethyl  $\gamma$ -Diethoxy-aceto-acetate**

**The Formation of Ethyl  $\alpha$ -Phthalimido-ethyl- $\gamma$ -diethoxy-aceto-acetate.**—Quite different was the behavior of this halide towards this sodium salt from that of the lower halide bromomethyl-phthalimide. The reaction was carried out in the usual way with 3.7 g. of sodium, 100 cc. of absolute alcohol and 20 g. of ethyl  $\gamma$ -diethoxy-aceto-acetate. The reaction was extremely sluggish and in order to hasten it 5 g. of potassium iodide was added to the solution. After heating on the steam-bath for 12 hours the solution finally became neutral to litmus and sodium bromide deposited, but there was no evidence of the separation of phthalimide as when bromomethyl-phthalimide was used. The alcohol was removed by distillation under diminished pressure and the oil finally extracted with ether, washed with water and dried over sodium sulfate. After removal of the ether we obtained 31 g. of a light red viscous oil which gave a strong test for nitrogen, and when subjected to distillation under diminished pressure decomposed with formation of a black, tarry mass. The crude oil was therefore carefully freed from the last traces of ether by heating in a high vacuum at 100° and then analyzed for nitrogen. The analysis gave results which indicated that the bromide had reacted normally with the sodium salt of the ketone ester giving the desired condensation product



*Analysis.* Calc. for  $C_{28}H_{38}O_7N$ : N, 3.56. Found: 3.24.

### Summary

1. An improvement in the method of preparation of bromomethyl-phthalimide has been described, and a description given of several new derivatives of methyl-phthalimide.

2. An attempt has been made to use this halide for the alkylation of ethyl aceto-acetate and ethyl  $\gamma$ -diethoxy-aceto-acetate but without success. The halide reacts abnormally with the sodium salt of  $\beta$ -ketone esters with formation of phthalimide.

3. The higher homolog, bromo-ethyl-phthalimide, reacts normally with  $\beta$ -ketone esters with formation of alkylation products containing nitrogen.

NEW HAVEN, CONNECTICUT

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF COLUMBIA UNIVERSITY]  
**RESEARCHES ON THIAZOLES. I. DERIVATIVES OF 2-PHENYL-BENZOTHAZOLE. SYNTHESIS OF AN ANALOG OF CINCHOPHEN (ATOPHAN)**

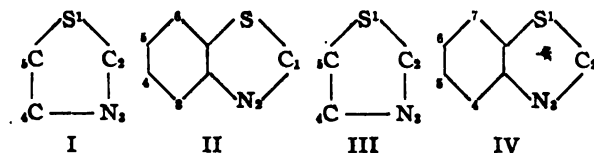
BY MARSTON T. BOGERT AND EMANUEL M. ABRAHAMSON

Received December 31, 1921

### Introductory

The Organic Laboratory of Columbia University has had under way for some time a number of investigations in the thiazole field, the results of which it hopes to publish as rapidly as opportunity permits.

The plan adopted for numbering the positions on the thiazole and benzothiazole nuclei both in Richter's "Lexikon" and in the Decennial Index to *Chemical Abstracts* is as indicated in Formulas I and II. This lack of uniformity seems to us highly undesirable and confusing. Therefore, we have employed consistently throughout this paper the numbering given in Formulas III and IV, so that S is always in position 1 and N at 3, while the C at 2 occupies the  $\mu$ -, or middle position. This is in agreement with the system adopted in the new (2nd) edition of Meyer-Jacobson's "Lehrbuch der organischen Chemie."<sup>1</sup>



For the experiments described in this first paper, 2-phenyl-benzothiazole has served as initial material, and from this interesting substance various derivatives have been prepared and studied.

Of the many methods of preparing this compound already given in the literature,<sup>2</sup> we have found fusion of benzanilide or benzaniline

<sup>1</sup> Vol. II, Part 3, Sec. 2, pp. 535 and 549.

<sup>2</sup> *Ber.*, 10, 2135 (1877); 12, 2360 (1879); 13, 8, 17, 1223, 1236 (1880); 15, 2033 (1882); 19, 1068, 1069 (1886); 23, 2476 (1890); 35, 1946 (1902); 44, 3037 (1911); 48, 1244, 1251 (1915). *Ann.*, 259, 301 (1890). *Am. Chem. J.*, 17, 1401 (1895). *Ger. pat.* 51,172 and 55,222; *Friedländer*, 2, 301, 302 (1891).

with sulfur the most satisfactory. This is the more economical and expeditious method, although the crude product is usually slightly colored.

Perhaps the most remarkable physical property of this thiazole, especially since it is an unoxidized sulfur compound, is its very agreeable odor, recalling that of tea roses or the rose geranium, so that it has been known also as "Rosenkörper." This odor has not been encountered in similar strength in any of its homologs or derivatives.

Our experiments have disclosed another peculiarity, namely, its failure to react, in solution in carbon disulfide, with aluminum chloride, so that neither the Friedel and Crafts nor Gattermann-Koch reaction is available for the production of derivatives. In both cases, the thiazole is recovered practically unaltered. Further experiments are under way in this direction, however, as it has been shown in other cases that carbon disulfide occasionally inhibits these reactions.

It is difficult to understand Hofmann's statement<sup>3</sup> that fuming nitric acid is without action upon 2-phenyl-benzothiazole, for we have found that this compound is nitrated with the greatest ease by fuming nitric acid, as well as by a mixture of nitric and sulfuric acids, to give nearly theoretical yields of the nitro compound. Hofmann<sup>3</sup> did nitrate it with mixed acids and obtained the same nitro derivative as that described by us (m. p. 188°). His analysis showed it to be a mononitro derivative, but he did not determine the position of the nitro group. Naegeli<sup>4</sup> also nitrated the compound with mixed acids with similar results. He then fused this nitro derivative with potassium hydroxide and from the melt separated a substance, m. p. 234–6°, soluble in sodium carbonate solution which was re-precipitated by mineral acid and could be reduced by tin and hydrochloric acid to an amino compound. These and other properties seemed to agree with those of *p*-nitrobenzoic acid (m. p. 238°). He states that the results of the fusion were very unsatisfactory, the yield of *p*-nitrobenzoic acid being poor, and that there was extensive decomposition and carbonization. On the basis of this result, he assigned the nitro group a position in the 2-phenyl radical *para* to the  $\mu$ -carbon of the thiazole nucleus. We have repeated Naegeli's experiments with the nitro compound, but were unable to isolate any crystalline products from the resultant tar.

Hofmann<sup>3</sup> noted that this nitro derivative could be readily reduced to a crystalline amine, whose hydrochloride was also crystalline<sup>5</sup>. Remy, Erhart and Co. state that this hydrochloride is difficultly soluble. The patent covers the azo dyes made from the amine, although no data whatever are given concerning the amine itself, or the method of its

<sup>3</sup> Hofmann, *Ber.*, 13, 1223 (1880).

<sup>4</sup> Naegeli, *Bull. soc. chim.*, [3] 11, 895 (1894).

<sup>5</sup> Ger. pat., 57,557; *Friedländer*, 3, 750 (1896).

preparation. We have found that reduction with tin and hydrochloric acid occurs smoothly and that the pure amine melts at  $207^{\circ}$  (corr.), whereas French patent 216,086<sup>6</sup> gives the melting point of *p*-aminophenyl-benzothiazole as  $154\text{--}155^{\circ}$ . There does not seem to be much doubt concerning the structure of the latter amine, since it was prepared by fusion of a mixture of aniline, *p*-toluidine and sulfur at  $180\text{--}250^{\circ}$ ; and its use for the manufacture of azo dyes was also patented.<sup>7</sup> It has also been shown that the nitration of amino benzothiazoles gives nitro derivatives with the nitro group in the benzothiazole benzene nucleus, and not in the 2-phenyl radical.<sup>8</sup>

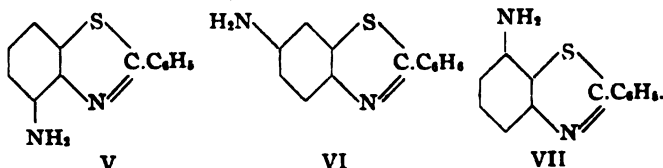
It appeared most unlikely, therefore, that direct nitration of 2-phenyl-benzothiazole would yield a derivative with its nitro group in the 2-phenyl nucleus. To prove the point, the amine was fused with caustic alkali, a reaction which proceeds much more smoothly than that with the corresponding nitro derivative. Benzoic acid itself was separated as the main product of this fusion. It follows from this that the amino group, and consequently the nitro group, must have been on the benzothiazole nucleus and not on the 2-phenyl nucleus.



A single attempt to isolate and identify the diamino-thiophenol, which should be the other main product of the fusion, was unsuccessful, and no further efforts were made, since the absence of any aminobenzoic was demonstrated, and this was deemed sufficient proof of the position of the nitro group.

As 5-amino-2-phenyl-benzothiazole has been described already,<sup>9</sup> and is not identical with the amine in question, the remaining possibilities are the 4-, 6- or 7-amino derivatives. The following experimental work led to a choice among these possibilities.

It has been observed frequently that an aromatic amine with free *para* and *ortho* positions, when treated with a diazonium salt under proper conditions, will couple twice, first in the *para* and then in the *ortho* position. Thus the 4- or 7-amino compound (V and VII) should couple twice, and the 6-amino derivative (VI) but once,



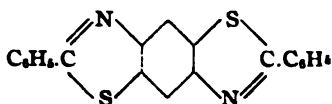
<sup>6</sup> *Winther*, 3, 379 (1910).

<sup>7</sup> Ger. pat. 79,214; *Friedländer*, 4, 829 (1899).

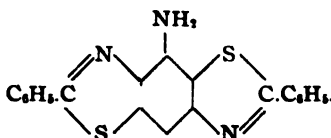
<sup>8</sup> Ger. pat. 81,711; *Friedländer*, 4, 831 (1899).

<sup>9</sup> *Kym, Ber.*, 32, 3534 (1899); Ger. pat. 75,674; *Friedländer*, 4, 825 (1899).

With diazotized *p*-nitro-aniline, the new amine was found to couple but once. The conclusion that it was, therefore, the 6-amino derivative was further corroborated by converting it into its benzal derivative and fusing the latter with sulfur, when a benzobisthiazole was obtained identical with that secured by Green and Perkin<sup>10</sup> from *p*-phenylenediamine dithiosulfonic acid and benzaldehyde, to which they assigned Formula VIII,



VIII



IX


This benzobisthiazole was also nitrated, the resulting nitro derivative reduced to the amine and the amine fused with caustic alkali. Only benzoic acid was isolated, and no aminobenzoic, thus locating the (nitro and) amino group on the middle benzene nucleus (IX).

No dinitro-2-phenyl derivatives were encountered in our experiments. Such compounds have been described, however,<sup>11</sup> and from them diamines (m. p. 192°, 208° and 255–256°) prepared, as well as azo dyes from the latter.<sup>12</sup>

6-Amino-2-phenyl-benzothiazole methylated under pressure with methyl alcohol and hydrochloric acid gave only the tertiary compound, but no quaternary salt. This reaction is being examined further, especially in its bearing upon the formation and tinctorial properties of the thioflavines.

By means of the Sandmeyer reaction, the amino compound was changed to the corresponding nitrile and the latter saponified to the acid (XIII).

Quinoline is stated to have very powerful antiseptic, antipyretic and antizymotic action, but is too toxic and causes collapse. Sulfur in cyclic union, as in thiophene, ichthyol, etc., in addition to its antiseptic and antiparasitic properties, causes a marked increase in resorption, resembling iodine in this respect, although in no way similar to that, pharmacologically. Cyclic compounds containing substituted sulfur also show striking analgesic properties which can be ascribed only to the entry of sulfur into such groups. Quinoline, itself, a strong protoplasmic poison, on fusion with

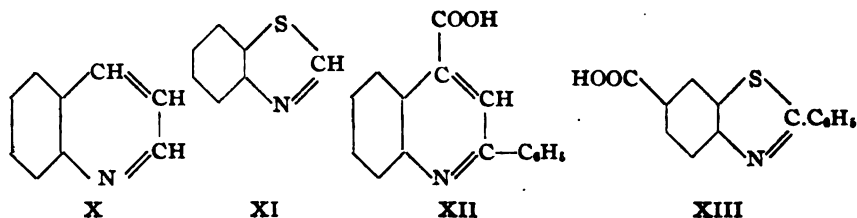
sulfur gives the so-called "thioquinanthrene,"  $\text{NC}_6\text{H}_4$    $\text{C}_6\text{H}_5\text{N}$ , which is inert physiologically. In cyclic systems, one sulfur atom appears to

<sup>10</sup> Green and Perkin, *J. Chem. Soc.*, 83, 1207 (1903).

<sup>11</sup> Ger. pat. 50,486; *Friedländer*, 2, 303 (1891); and 54,921; *Friedländer*, 2, 305 (1891).

<sup>12</sup> See also Ger. pat. 58,641; *Friedländer*, 3, 765 (1896).

have much the same effect as an ethylene group,  $-\text{CH}:\text{CH}-$ , an analogy well illustrated by comparison of corresponding members of the benzene and thiophene series. The benzothiazoles (XI) are, therefore, the parallels to the quinolines (X), and show many striking points of similarity in their chemical behavior. Hence, the new acid noted above (XIII) may show some of the valuable properties of the well-known  $\alpha$ -phenyl-cinchoninic acid (Cinchophen, or Atophan) (XII) as a remedy for gout. If the presence of sulfur in the complex should really prove to increase resorption, this should be a valuable adjunct to a uric acid eliminant. It is hoped to test experimentally its therapeutic possibilities.



According to Ciusa and Luzzatto<sup>13</sup> most of the physiological action of 2-phenyl-cinchoninic acid is due to the 2-phenyl group, and this appears to be borne out by the fact that the following compounds show practically the same effect as cinchophen itself: its methyl or ethyl (Acitrin) esters, 6-methyl-2-phenyl-cinchoninic acid (Paratophan), the methyl (Novatophan K) or ethyl (Neocinchophen, Novatophan) esters of the latter, 8-methoxy-2-phenyl-cinchoninic acid (Isatophan), cinchophen salicylate, 2-phenylquinoline-4-diethyl carbinol, 2-phenyl- $\beta$ -naphthoquinoline- $\gamma$ -carboxylic acid (Diapurin), while cinchoninic acid, itself, is inactive. Modifications of the 2-phenyl group by substitution of H by OH, OR or  $\text{NR}_2$  groups, seems to reduce the usefulness of the drug. The 2'- $\text{COOH}$  derivative prepared by Reissert and Holle<sup>14</sup> in 1911 is therefore likely to show a different behavior physiologically from that of the isomer carrying the  $\text{COOH}$  group on the other benzene nucleus, even though the main function of this group is simply to render the complex more easily soluble. No record has been found of any physiological experiments with the product described by Reissert and Holle; it was not prepared with any such object in view, since it was merely incidental to a study of thio-phthalanil.

In acetic acid solution, 2-phenyl-benzothiazole takes up 4 atoms of bromine per mole of thiazole; red crystals of the tetrabromo addition product  $\text{C}_{13}\text{H}_9\text{NSBr}_4$  separate. This behavior parallels that of the analogous selenium compound, which also adds 4 bromine atoms. Fromm and

<sup>13</sup> Ciusa and Luzzatto, *Atti accad. Lincei*, [5] 22, I, 305 (1913); *Gazz. chim. ital.*, 44, I, 64 (1914); *Zentr.*, 1913, II, 1318.

<sup>14</sup> Reissert and Holle, *Ber.*, 44, 3035 (1911)..

Martin<sup>18</sup> assigned the structure  $\text{C}_6\text{H}_5 \begin{array}{c} \diagup \text{N}(\text{Br}_2) \\ \diagdown \text{Se}(\text{Br}_2) \end{array} \text{C} \cdot \text{C}_6\text{H}_5$  to the product,

basing this conclusion on the ease with which the bromine could be displaced and the parent selenazole regenerated. The bromine addition product of 2-phenyl-benzothiazole is less stable than the corresponding selenazole compound, since it loses bromine even on standing at ordinary temperature. This is in line with the lower basicity of sulfur. When heated in 2:1 acetic acid, the solution suddenly turns colorless and white crystals of a monobromo substitution product,  $\text{C}_{12}\text{H}_8\text{NSBr}$ , are deposited as the solution cools. This bromo derivative was proved to be the 6-bromo compound by preparing the same substance from the 6-amino derivative through the diazo reaction. This is similar to the transition of benzaniline dibromide to benzal *p*-bromo-aniline and hydrochloric acid.<sup>19</sup>

Iodine also forms an unstable addition product with 2-phenyl-benzothiazole, from which sodium thiosulfate removes the halogen quantitatively, thus affording a convenient method of analysis. Unlike the analogous selenazole, only 2 atoms of iodine are added per mole of thiazole, instead of 4, a behavior also in harmony with the weaker basicity of sulfur. As this addition product contains about 50% of iodine by weight, it offers possibilities as an iodoform substitute, since it may combine the action of nuclear sulfur with that of the iodine.

Like quinoline, 2-phenyl-benzothiazole dissolved in toluene adds acetyl chloride readily; the product is decomposed immediately by water or on application of heat.

Other experimental work under way with this thiazole relates to its reduction, the behavior of the 6-amino derivative when subjected to such ordinary aniline reactions as lead to the corresponding quinoline, the cinchophen (Atophan) (*i. e.*, from the 6-benzalamino derivative and pyruvic acid), the phenol, various dyes, etc., and will be reported later.

### Experimental Part

**2-Phenyl-benzothiazole,  $\text{C}_{12}\text{H}_8\text{NS}$ .**—(a). From Benzanilide.—The Hofmann process<sup>3</sup> was employed with a few modifications. Five hundred g. of benzanilide and 200 g. of sulfur (2.5 equivalents) were fused together at 250–280° until evolution of steam ceased. The melt was then distilled under diminished pressure from 2 Pyrex flasks with side tubes sealed together. The main distillate which came over at 220° at 19 mm. was cooled, pulverized and boiled for an hour under a reflux condenser with one liter of hot conc. hydrochloric acid. The yellow acid extract was filtered hot through asbestos, and the filtrate added to 6 liters of cold water. After the precipitated thiazole was crystallized from alcohol, it melted at 114° (corr.). Yield, 400 g. or 75%.

<sup>18</sup> Fromm and Martin, *Ann.*, **401**, 1781 (1913).

<sup>19</sup> Hantzsch, *Ber.*, **23**, 2774 (1890).



(b). From Benzaniline.—This is also a modification of a method already in the literature.<sup>17</sup> Five hundred g. of benzaniline, prepared by mixing equal moles of benzaldehyde and aniline and heating the mixture at 120–130° until all water was removed, was heated with 200 g. of sulfur (2.25 equivs.) at 250–260° until no more hydrogen sulfide was evolved, and the heating then continued for 2 hours longer under reduced pressure. The crude melt, purified as above, gave a yield of pure product (m. p. 114°) amounting to 375 g. or 64%. With either of the above methods, when the temperature rises much higher than that given the yield is diminished considerably. Distillation under diminished pressure is the quickest way to secure a colorless product, but is troublesome. The substance obtained by extracting the crude melt directly with hot conc. hydrochloric acid, when purified as indicated above, melts at practically the same point (114°), although it often has a pale yellowish cast. For most purposes, therefore, the undistilled product is entirely suitable.

The second method has been found to be the more rapid, economical and convenient, although the crude product from benzanilide is apt to be rather lighter in color.

6-Nitro-2-phenyl-benzothiazole,  $C_{12}H_7NS(NO_2)$ .—After 21 g. (0.1 mole) of the thiazole was added slowly to 150 cc. of fuming nitric acid (sp. gr. 1.60), the solution was allowed to stand for half an hour and then poured into 500 cc. of cold water. The precipitated nitro derivative was collected and crystallized from glacial acetic acid. M. p. 188° (corr.). Yield, 24 g., or 94%.

In another series of experiments we followed in the main the process of Naegeli.<sup>4</sup> Twenty one g. of the thiazole was dissolved in 100 cc. of conc. sulfuric acid. This solution was stirred and the temperature kept at 75° while a mixture of 15 g. (0.12 mole) of conc. nitric acid and 20 g. of conc. sulfuric acid was added drop by drop. The stirring was continued for half an hour after all of the nitric acid had been added. Then the mixture was heated at 100° for an hour, allowed to cool, poured into 1500 cc. of cold water, the precipitate collected and crystallized from glacial acetic acid as yellow needles, m. p. 188° (corr.); yield, 25 g., or 98%. Both Hofmann<sup>3</sup> and Naegeli<sup>4</sup> give the melting point as 188°.

FUSION OF THE NITRO DERIVATIVE WITH CAUSTIC ALKALI.—Ten g. of this nitro compound, 20 g. of potassium hydroxide and 40 g. of water, were heated together for 15 minutes at 200–210°. After cooling the solution, it was diluted, the tar removed and the filtrate acidified. A trace of colorless solid separated, insufficient to recrystallize or purify; it did not melt sharply but began to soften in the vicinity of 100°. Naegeli believed that he isolated *p*-nitrobenzoic acid (m. p. 238°) from this material but we failed to confirm this, although 4 times as much initial material was used by us.

6-Amino-2-phenyl-benzothiazole,  $C_{12}H_8NS(NH_2)$ , (Formula VI).—Twenty-five and six-tenths g. (0.1 mole) of nitro derivative and 40 g. (0.33 mole) of granular tin were covered with 150 cc. of conc. hydrochloric acid, and the flask warmed to start the reaction. The reduction proceeded with evolution of so much heat that it was necessary to chill the flask. On completion of the reduction the solution was allowed to cool and crystals of the double tin salt separated. The mixture was made strongly alkaline, the precipitated base collected, washed with 3 *N* sodium hydroxide solution (to remove tin salts) and then with water. The crude base, crystallized from aniline and finally from toluene, gave colorless needles, m. p. 207° (corr.); yield, 16 g. or 71%.

*Analyses.* Calc. for  $C_{12}H_{10}N_2S$ : N, 12.39. Found: 12.34, 12.43.

This amine is practically insoluble in water, in dilute acids, or in concentrated hydrochloric acid; difficultly soluble in methyl, in ethyl or in *iso*-amyl alcohol, ethyl or *iso*-amyl acetate, chloroform, carbon tetrachloride, benzene or toluene, and still more difficultly soluble in ether. Dilution with ether generally precipitates it from solution

<sup>17</sup> Ziegler, *Ber.*, 23, 2476 (1890); Ger. pat. 51,172; Friedländer, 2, 301 (1891).

in other solvents. Its alcoholic solutions show a beautiful blue fluorescence, and even ether takes up sufficient to show this fluorescence, too.

**ACETYL DERIVATIVE.**—From the base and acetic anhydride the acetyl derivative crystallizes in cubes, m. p.  $214^{\circ}$  (corr.).

*Analyses.* Calc. for  $C_{15}H_{12}ON_2S$ : N, 10.43. Found: 10.49, 10.57.

**FUSION OF THE AMINE WITH CAUSTIC ALKALI.**—Fifteen g. of amine and 60 g. of moist potassium hydroxide were fused for 15 minutes at as low a temperature as possible. The cool melt was dissolved in water, filtered, the filtrate acidified, and the precipitate crystallized from water. It melted at  $122^{\circ}$ , and was free from nitrogen and sulfur. Mixed with pure benzoic acid, the melting point remained unchanged. Some of it was dissolved in absolute alcohol, the solution saturated with dry hydrogen chloride, and water then added. Upon treatment with sodium carbonate solution, oily droplets separated which had the odor characteristic of ethyl benzoate.

***p*-Nitrobenzene-azo-(6-amino-2-phenyl-benzothiazole),**  $O_2N.C_6H_4.N:N.C_{12}H_7NS.(NH_2)$ .—Two and three-quarters g. of *p*-nitro-aniline was diazotized and the solution poured into a suspension of 4.5 g. of the aminothiazole in 100 cc. of 1:10 g. hydrochloric acid. The mixture was cooled and stirred for an hour; then the brown precipitate was collected, washed with water, crystallized from aniline, and the aniline removed by dil. hydrochloric acid. Red needles, melting at  $196^{\circ}$  (corr.) were obtained. They were difficultly soluble in aniline or in nitrobenzene, and practically insoluble in most other organic solvents; yield, 5 g., or 67%.

*Analyses.* Calc. for  $C_{19}H_{15}O_2N_4S$ : N, 18.67. Found: 18.70, 18.75.

**ATTEMPTED FURTHER COUPLING.**—Two and three-quarters g. of *p*-nitro-aniline was diazotized and allowed to act upon the amine as before. To this solution, an equal amount of diazotized *p*-nitro-aniline was added, while the temperature was kept below  $5^{\circ}$  and the mixture was stirred vigorously for half an hour. The brown precipitate obtained by the first coupling remained unchanged. The mixture was then filtered and the filtrate divided into two parts. The precipitate was washed thoroughly with water and crystallized from aniline, when it melted at  $194$ – $195^{\circ}$  (corr.). Mixed with the product from the previous experiment, the melting point was  $195^{\circ}+$  (corr.). One part of the filtrate from the brown precipitate was made alkaline, but no change was observed. The other portion was added to an alkaline solution of phenol, causing an immediate intense red color and the formation of an orange precipitate on acidification, which proved the presence of unaltered diazo-*p*-nitro-aniline. Hence, the original amine couples but once.

**ACETYL DERIVATIVE.**—This was obtained from the azo derivative and acetic anhydride as golden-yellow plates, m. p.  $203^{\circ}$  (corr.).

*Analyses.* Calc. for  $C_{21}H_{15}O_2N_4S$ : N, 16.01. Found: 16.01, 15.74.

**6-Benzalamino-2-phenyl-benzothiazole,**  $C_6H_5.CH:N.C_{12}H_7NS$ .—Twenty-two and six-tenths g. (0.1 mole) of aminothiazole was suspended in 150 cc. of alcohol, 15 cc. (0.15 mole) of benzaldehyde added and the mixture boiled gently for an hour; the solution boiled with bone black, filtered and cooled gave pale yellow plates, m. p.  $151^{\circ}$  (corr.); yield, 30 g., or 96%.

*Analyses.* Calc. for  $C_{20}H_{14}N_2S$ : N, 8.92. Found: 8.98, 8.81.

It is practically insoluble in water, and difficultly soluble in alcohol, ethyl or *iso*amyl acetate, ether, chloroform, carbon tetrachloride, acetic acid, benzene or toluene.

**2,2'-Diphenyl-benzobisthiazole (Formula VIII).**—Twenty g. of this benzalamino derivative was fused with 10 g. (5 equivalents) of sulfur for 4 hours at  $250$ – $60^{\circ}$ , and the heating then continued for an hour longer under diminished pressure. The cold melt was pulverized, and extracted repeatedly with hot conc. hydrochloric acid. The acid

extract (200 cc.) was poured into 1 liter of water, and the precipitate collected and crystallized from acetic acid giving pale yellow needles, m. p. 235° (corr.); yield, 7 g. or 32%.

*Analyses.* Calc. for  $C_{20}H_{12}N_2S_2$ : N, 8.14. Found: 8.08, 8.17.

Green and Perkin<sup>10</sup> prepared a diphenyl-benzobisthiazole, from *p*-phenylenediamine dithiosulfonic acid and benzaldehyde, which crystallized from amyl alcohol in pale straw colored needles, m. p. 232–4°, and which appears to be identical with the compound described above.

**4-Nitro-2,2'-diphenyl-benzobisthiazole**,  $O_2N.C_{20}H_{11}N_2S_2$ .—Five g. of the above bisthiazole was dissolved in 20 cc. of conc. sulfuric acid, 3 cc. of conc. nitric acid added slowly, the solution left at room temperature for half an hour, then heated at 100° for an hour, cooled, and poured into 200 cc. of ice water. The yellow precipitate was collected, crystallized from nitrobenzene, washed with methyl alcohol (to remove the solvent) and dried giving a yield of 4 g., or 70% of yellow needles, m. p. 262° (corr.). The substance is difficultly soluble or insoluble in methyl, ethyl or *iso*amyl alcohol, ethyl or *iso*amyl acetate, ether, acetic acid or anhydride, chloroform or carbon tetrachloride, benzene, toluene or xylene.

*Analyses.* Calc. for  $C_{20}H_{11}O_2N_3S_2$ : N, 10.80. Found: 10.93, 10.95

**4-Amino-2,2'-diphenyl-benzobisthiazole** was prepared by boiling 3 g. of the nitro compound for several hours with 3.5 g. of tin and 30 cc. of conc. hydrochloric acid, until the reduction was complete. The solution was made strongly alkaline with sodium hydroxide, the precipitated base collected on a filter, crystallized from aniline, the crystals were washed free from aniline by dil. hydrochloric acid, then washed with dil. ammonia and dried over conc. sulfuric acid. A yield of 2 g., or 72%, of yellowish needles was obtained; m. p. 285–287° (corr.).

*Analyses.* Calc. for  $C_{20}H_{13}N_3S_2$ : N, 11.70. Found: 11.93, 11.98.

**ACETYL DERIVATIVE.**—This was obtained from the amine and acetic anhydride and forms colorless plates, m. p. 250–253° (corr.).

*Analysis.* Calc. for  $C_{22}H_{15}ON_2S_2$ : N, 10.47. Found: 10.62.

**FUSION OF THE AMINE WITH CAUSTIC ALKALI.**—One g. of this amine was fused with 4 g. of moist potassium hydroxide at a low temperature for 10 minutes, the melt allowed to cool, dissolved in 25 cc. of water, filtered and the filtrate acidified with hydrochloric acid. The precipitate obtained was removed and crystallized from water. It proved to be benzoic acid (m. p. 122°). The filtrate was neutralized with ammonia, evaporated to dryness on the water-bath, the residue warmed with 5 cc. of acetic anhydride, the solution filtered through glass wool, and the filtrate carefully diluted. No acetamino-benzoic acid was obtained. Therefore the amino group must have been on the central benzene nucleus and not on either the 2- or 2'-phenyl nucleus.

**6-Dimethylamino-2-phenyl-benzothiazole**,  $(CH_3)_2N.C_{12}H_8NS$ .—Ten g. of 6-amino-2-phenyl-benzothiazole, 6 cc. of conc. hydrochloric acid and 20 cc. of absolute methyl alcohol were heated together in a sealed tube at 175° for 24 hours. The tube then contained a red viscous liquid which, on standing, deposited reddish-brown needles which were recrystallized from acetone and then melted at 185 (corr.); yield, 4 g., or 36%.

*Analyses.* Calc. for  $C_{14}H_{14}N_2S$ : N, 11.03. Found: 11.21, 11.11.

No methyl chloride addition product was found.

**2-Phenyl-benzothiazole Tetrabromide**,  $C_{12}H_7NSBr_4$ .—Ten g. of 2-phenyl-benzothiazole was dissolved in 250 cc. of acetic acid, 10 cc. of bromine (2 molec. equivalents) added, the mixture shaken vigorously for 10 minutes and allowed to stand for half an hour. Red needles separated which were collected and dried over potassium hydroxide

*in vacuo*. The compound is quite unstable, giving off bromine on standing. The crystals were therefore dried for only half an hour. The substance melted in the neighborhood of  $125^{\circ}$ , with considerable decomposition; yield, 15 g., or 60%.

*Analyses.* Calc. for  $C_{12}H_8NSBr_4$ : N, 2.64; Br, 60.22. Found N, 2.68, 2.80; Br, 59.95.

Bromine was determined by adding the sample to a very dilute sodium hydrogen sulfite solution, filtering out the liberated 2-phenyl-benzothiazole, acidifying the filtrate and precipitating the bromine ion as silver bromide.

**6-Bromo-2-phenyl-benzothiazole**,  $Br.C_{12}H_8NS$ .—In a subsequent experiment for the preparation of the above tetrabromide, the acetic acid solution of the thiazole (10 g.) and bromine (10 cc.) was diluted with 150 cc. of water and warmed to complete the solution. The effect of this dilution and warming, however, caused a sudden change in the course of the reaction; the red color of the solution disappeared, with evolution of bromine, and a colorless solid separated which crystallized in plates as the material cooled. These were recrystallized from acetic acid, and proved to be a monobromo substitution product, m. p.  $152^{\circ}$  (corr.); yield, 13 g., or 94%.

*Analyses.* Calc. for  $C_{12}H_8NSBr$ : C, 53.79; H, 2.78; N, 4.83; S, 11.05; Br, 27.55. Found: C, 54.44; H, 3.03; N, 4.79; S, 11.08; Br, 27.28.

The results of nitration led us to infer that the bromine also had entered Position 6 on the nucleus. In order to confirm this conclusion 11.3 g. (0.05 mole) of the 6 amino derivative was suspended in a mixture of 50 cc. of water and 10 cc. of conc. sulfuric acid at  $0^{\circ}$ , and 4 g. of sodium nitrite (0.05 mole) dissolved in 20 cc. of water added slowly while the mixture was cooled and stirred mechanically. When the diazotization was completed, 25 g. of potassium bromide was added and then (very slowly) 10 g. of copper powder. The ice-cold solution was gradually heated to boiling and kept at this temperature for half an hour; then it was cooled, the precipitated bromo derivative collected and crystallized twice from acetic acid, when it melted at  $152^{\circ}$  (corr.). Mixed with the compound obtained above from the tetrabromide, the melting point remained unaltered; yield, 3 g., or 21%.

*Analysis.* Calc. for  $C_{12}H_8NSBr$ : N, 4.83. Found: 4.89.

**2-Phenyl-benzothiazole-di-iodide**,  $C_{12}H_8NSI_2$ .—Twenty-one and one-tenth g. (0.1 mole) of 2-phenyl-benzothiazole was dissolved in acetic acid and a solution of 50.8 g. (0.2 mole) of iodine in the same solvent was added. The mixture was shaken for half an hour and then allowed to stand for several hours. A trace of crystalline material separated. An additional 21.1 g. of thiazole was then introduced. The solution soon deposited a large amount of glistening black needles, which were removed, washed with acetic acid, then with water, and dried over potassium hydroxide under diminished pressure, when they melted at  $84.5^{\circ}$  (corr.); yield, 78 g., or 85%.

*Analyses.* Calc. for  $C_{12}H_8NSI_2$ : I, 54.58. Found: 55.05, 54.98.

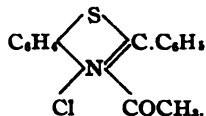
This addition product is quite unstable, and sodium thiosulfate removes its iodine quantitatively.

**6-Cyano-2-phenyl-benzothiazole**,  $NC.C_{12}H_8NS$ .—Fifty g. of cupric sulfate pentahydrate was dissolved in 100 cc. of warm water, a solution of 55 g. of potassium cyanide in 100 cc. of water was added, the mixture was heated to boiling and a suspension of the diazotized amine (prepared by adding a solution of 14 g. of sodium nitrite in 50 cc. of water to a suspension of 45.3 g. of amine in a mixture of 150 cc. of water and 50 cc. of hydrochloric acid and stirring for half an hour) added very slowly with active stirring. The mixture was boiled for half an hour longer, cooled and the precipitated nitrile collected. It is difficultly soluble or insoluble in ethyl or *iso*amyl alcohol or acetate, benzene, toluene or xylene, nitrobenzene, acetic acid, chloroform or carbon tetrachloride, and no good crystallizing medium was found for it.

**2-Phenyl-benzothiazole-6-carboxylic Acid**, (Formula XIII),  $C_{15}H_9NS.COOH$ .—The crude nitrile obtained above was boiled under a reflux condenser with a mixture of 100 cc. of conc. sulfuric acid and 60 cc. of water, until a test portion dissolved completely in dil. sodium hydroxide (about 15 hours). The solution was then cooled, poured into 2 liters of cold water and the precipitated acid removed. As no satisfactory neutral solvent could be found for crystallizing, it was dissolved in dil. sodium hydroxide and converted into the methyl ester by adding 50 g. (0.4 mole; twice the calculated amount) of dimethyl sulfate drop by drop, with simultaneous addition of sufficient dil. sodium hydroxide solution to keep the solution faintly alkaline. After stirring the mixture for an hour to insure destruction of all of the excess of dimethyl sulfate the separated thiazole methyl ester was filtered out, dissolved in alcohol, the solution boiled with bone black, and the ester crystallized to constant melting point, giving minute prisms of pale yellowish tinge, m. p.  $153-154^\circ$  (corr.); yield, 7 g., or 13%.

*Analyses.* Calc. for  $C_{15}H_{11}O_2NS$ : N, 5.20. Found: 5.11, 5.50.

This purified ester was saponified by boiling 6 g. of it with 200 cc. of 10% aqueous sodium hydroxide until all of it had dissolved. The hot solution was then boiled with bone black, filtered, the filtrate acidified with hydrochloric acid, the precipitated thiazole acid removed, washed and dried at  $120^\circ$  giving a slightly grayish powder, m. p.  $261-263^\circ$  (corr.) with decomposition; yield, 5 g., or 88% calculated to the ester, or 11% calculated back to the original amine.



**Acetyl Chloride Addition Product of 2-Phenyl-benzothiazole**,  $C_{15}H_9NS.Cl.COCH_3$ .—On adding 5 g. of acetyl chloride to a solution of 5 g. of 2-phenyl-benzothiazole in 25 cc. of toluene, white leaflets of the addition product separated, amounting to 5 g. (73%). The substance lost the acetyl chloride very easily when it was warmed, so that the melting point obtained is that of the thiazole itself ( $114^\circ$ ).

It was analyzed by agitating it with water, filtering out the precipitated thiazole, and determining the chlorine in the filtrate with silver nitrate.

*Analyses.* Calc. for  $C_{15}H_{11}ONSCl$ : Cl, 12.24. Found: 11.98, 12.19.

### Summary

1. An improved method is given for the preparation of 2-phenyl-benzothiazole in considerable quantities.
2. The product obtained by nitration of 2-phenyl-benzothiazole is shown to be the 6-nitro derivative by conversion, through the amine and its benzal derivative, into 2, 2'-diphenyl-benzobisthiazole. Hitherto the nitro group has been assigned position 4' on the 2-phenyl nucleus.
3. The position of the amine group was further established by coupling it but once with diazotized *p*-nitro-aniline.
4. Nitro and amino derivatives of the 2,2'-diphenyl-benzobisthiazole were prepared and the positions of the groups determined.
5. 2-Phenyl-benzothiazole adds 4 bromine atoms directly. The tetrabromide lost bromine and hydrogen bromide when boiled with dil. acetic acid to form 6-bromo-2-phenyl-benzothiazole, which was also produced from the 6-amino derivative. With iodine, only 2 atoms are taken up; an unstable di-iodide results.

6. The addition product of 2-phenyl-benzothiazole and acetyl chloride loses acetyl chloride readily when heated or on treatment with water.

7. 6-Amino-2-phenyl-benzothiazole was changed into the cyanide, and the latter into the 6-carboxylic acid, which is structurally analogous to Cinchophen (Atophan), and which it is hoped may show useful therapeutic properties.

NEW YORK, N. Y.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, NOTRE DAME UNIVERSITY]

## ACETYLENE COMPOUNDS WITH SILVER PHOSPHATE AND SILVER ARSENATE

By P. BENEDICT OBERDOERFER AND J. A. NIEUWLAND

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Unlike the mercury and copper derivatives, silver compounds of acetylene prepared by passing the gas into acid solutions of various silver salts are usually the explosive acetylides or carbides of the metal, but in the case of the phosphate of silver dissolved in phosphoric acid, a compound is formed that is very stable.

This substance prepared by Nieuwland and Maguire<sup>1</sup> is not notably affected by light and is not an aldehyde derivative. The formula  $3(C_2Ag_2) \cdot 2H_3PO_4 \cdot Ag_3PO_4 \cdot H_2O$  was applied to the substance, but apparent discrepancies in relationship of analytical results and formula suggested that it might be advisable to go over the matter again with a view of ascertaining whether the original determinations were correct.

Acetylene silver phosphate was prepared according to the method used by Nieuwland and Maguire. Chemically pure silver nitrate which had been recrystallized was treated with chemically pure dibasic sodium phosphate until an excess of the phosphate was present. The yellow silver phosphate was carefully washed by decantation until all traces of disodium phosphate and silver nitrate were removed; it was then filtered by suction and treated with a strong solution of phosphoric acid, and after all had dissolved, saturated with purified acetylene. A cream colored substance was precipitated, which was washed 10 or 12 times by decantation until test showed absence of free phosphoric acid. After being filtered by suction it was dried in an air-bath and desiccator alternately, until repeated weighings showed no more loss.

Four analyses were made. In the first two operations the silver was determined as silver chloride and the filtrates from the silver chloride were used to estimate the amount of phosphate present as magnesium pyrophosphate. In the third and fourth operations the compound was analyzed electrolytically. From the results obtained a formula was cal-

<sup>1</sup> Nieuwland and Maguire, *THIS JOURNAL*, **28**, 1025 (1906).

culated, which answered to the following percentages, agreeing very closely with the values obtained.

Calc.: Ag, 77.95; PO<sub>4</sub>, 8.58. Found: Ag, 78.27, 77.72, 77.85, 77.02, Av. 77.92; PO<sub>4</sub>, 8.49, 8.26, Av. 8.38.

The average value for silver differs only 0.03% from the theoretical value, while the difference for PO<sub>4</sub> is 0.2%. The formula which was established on the basis of these results is 6(AgCCH).Ag<sub>2</sub>HPO<sub>4</sub>.

The reaction proceeds probably in the following manner,



This formula is completely at variance with the formula calculated by Nieuwland and Maguire. It seems evident that they had not succeeded in removing all free phosphoric acid, and had not dried the precipitate carefully enough.

Acetylene silver arsenate was prepared by the same method as the compound described above, using the same precautions to free the cream colored substance from every trace of free arsenic acid, and then from water by prolonged drying in a steam-oven and desiccator alternately until successive weighings showed no loss.

The silver was estimated as silver chloride. In the first two operations the substance was dissolved in dil. nitric acid; in the next two operations it was dissolved in aqua regia; in the other cases it was dissolved in conc. nitric acid. In all there were made 7 determinations, taking the precaution to dissolve the precipitated silver chloride in ammonia and reprecipitate it by nitric acid before drying and weighing.

In the estimation of the arsenic content of the compound, the procedure was in general the method worked out by Gooch. Six determinations were made in all. For the first duplicates the filtrates from the silver chloride precipitates were evaporated to dryness, treated with hydrochloric acid and water and then reduced by potassium iodide and sulfuric acid to arsenious acid according to the equation,  $\text{H}_2\text{AsO}_4 + 2\text{KI} + \text{H}_2\text{SO}_4 \longrightarrow \text{H}_2\text{AsO}_3 + \text{H}_2\text{O} + \text{K}_2\text{SO}_4$ . After the liquid had been diluted to 100 cc. and then boiled down to 40 cc. to drive off most of the free iodine, the remaining free iodine was cautiously bleached by sulfurous acid, the solution at once diluted, nearly neutralized with potassium carbonate, and completely with sodium hydrogen carbonate; it was then titrated against a standardized iodine solution, the starch indicator being added shortly before the end-point was reached to insure a deep blue coloration.

The second duplicate of determinations was made by dissolving the substance in conc. hydrochloric acid to which 1 cc. of conc. nitric acid had been added, filtering from the silver chloride precipitates, and treating again according to Gooch's method. The third duplicate of determinations was made according to the modifications of Gooch's method by

Geo. Ross Robertson<sup>2</sup> for the estimation of arsenic in arsphenamine and allied products. In this case the silver iodide precipitated by the addition of potassium iodide was not filtered off, but the titration was made after treating the mixture as in the previous determinations.

Calculation of the molecular formula according to the results obtained for silver and arsenic presented great difficulties. It had been assumed that a molecule of silver arsenate might combine with 1, 2 or 3 molecules of acetylene. The percentage of silver found was, however, in each instance too high, while that of arsenic seemed to be too low. Comparison with the acetylene silver phosphate compound described above, as well as the fact that the acetylene silver arsenate puffed up on being heated, pointed to the possibility of the compound being a mixture, and a calculation made on this assumption gave the following result, with which those of the various analyses agreed very closely.

Calc.: Ag, 69.57; As, 13.08. Found: Ag, 69.46, 69.39, 69.06, 69.19, 69.83, 69.28, 69.47, Av. 69.38; As, 12.58, 12.63, 12.47, 12.57, 12.72, 12.61, Av. 12.66.

The average result for silver is within 0.19% of the calculated value; that of arsenic within 0.48%. The formula may therefore be written,  $2(\text{H}_3\text{AsO}_4) \cdot \text{Ag}_3\text{AsO}_4 \cdot 4\text{C}_2\text{Ag}_2$ . The equation for this particular reaction may be written,  $2 \text{Ag}_3\text{AsO}_4 + 3(\text{C}_2\text{H}_2) \longrightarrow 3 \text{C}_2\text{Ag}_2 + 2 \text{H}_3\text{AsO}_4$ ; and for the entire reaction thus,



The properties of acetylene silver arsenate are analogous to those of acetylene silver phosphate described by Nieuwland and Maguire. When the arsenate was exposed to direct sunlight, it changed from a cream color to a purplish-violet in a short time. In diffused daylight it took several days for a change in color to become noticeable; it did not give up aldehyde as in the case of the acetylene compound of mercuric chromate prepared by the authors mentioned above, nor did it respond to the iodoform reaction, but an iodine derivation of acetylene was formed, which could be recognized by its characteristic odor. The compound is insoluble in ammonia, alcohol and ether, but very soluble in potassium cyanide with decomposition, acetylene being evolved. When heated to about 400°, it deflagrated quietly, and in this regard it differs, like acetylene silver phosphate, from other silver acetylene compounds.

### Summary

1. The correctness of the formula of acetylene silver phosphate prepared and described by J. A. Nieuwland and J. A. Maguire was tested, and it was found that their formula was defective owing to the presence of free phosphoric acid and water which had not been removed. Analytical results assign the following formula to the compound:  $6(\text{AgCCH}) \cdot \text{Ag}_3\text{HPO}_4$ .

<sup>2</sup> Robertson, *TECH JOURNAL*, 43, 182 (1921).



2. Acetylene silver arsenate was prepared according to the method used for acetylene silver phosphate. The analysis of the compound points to the following formula:  $2(\text{H}_3\text{AsO}_4) \cdot \text{Ag}_2\text{AsO}_4 \cdot 4\text{C}_2\text{Ag}_2$ .

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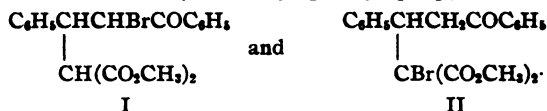
[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF HARVARD UNIVERSITY]

## THE ACTION OF BROMINE ON CERTAIN DELTA KETONIC ESTERS

By E. P. KOHLER

Received January 9, 1922

When bromine acts on  $\delta$ -ketonic esters of the type obtained by adding malonic esters to  $\alpha, \beta$  unsaturated ketones it replaces one hydrogen atom with the greatest ease.<sup>1</sup> In the cold the bromination stops sharply at this point. If the reaction is carried out in chloroform or carbon tetrachloride it invariably gives a mixture of 2 isomeric monobromo compounds in nearly equal amounts. As both of these readily lose hydrogen bromide and form a cyclopropane derivative<sup>2</sup> the bromine in each must be either in the  $\alpha$ - or the  $\gamma$ -position. Thus the only possible formulas for the products obtained from dimethyl-benzoyl-phenyl-propylmalonate are,



Since the  $\gamma$ -bromo compound has 2 dissimilar asymmetric carbon atoms, the 2 bromo compounds may be stereo-isomeric forms represented by Formula I, or one may be a  $\gamma$  derivative and the other the  $\alpha$  derivative represented by Formula II. When these substances were first encountered it was assumed that they were stereo-isomers because, on treatment with reagents that do not cause isomeric change, both gave the same unsaturated compound.<sup>3</sup> Later investigations<sup>4</sup> showed that this unsaturated compound in reality is a cyclopropane derivative which in nearly all respects behaves like an ethylenic compound. Although the cyclopropane derivative might be formed from an  $\alpha$ - as well as from a  $\gamma$ -bromo compound, it nevertheless seemed most probable that the two substances were stereo-isomers. As the substances are formed in nearly equal amounts structural isomerism implied that the  $\alpha$ - and  $\gamma$ -hydrogen atoms were replaceable with equal ease and if this were the case there seemed to be no adequate reason why the reaction should stop so sharply with the replacement of one hydrogen atom.

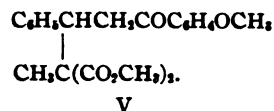
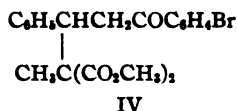
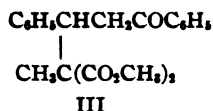
<sup>1</sup> *Am. Chem. J.*, **46**, 482 (1911).

<sup>2</sup> *THIS JOURNAL*, **39**, 1410 (1917).

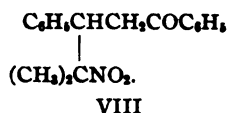
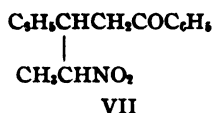
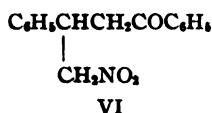
<sup>3</sup> *Ref. 1*, p. 483.

<sup>4</sup> *Ref. 2*, p. 1404.

Doubt as to the validity of this reasoning arose when it was discovered that while bromination in methyl alcohol that had been previously saturated with hydrogen bromide gave only the lower melting bromo derivative, it was not possible to transform the higher into the lower-melting compound by digestion with methyl alcoholic hydrobromic acid. It was found also, that when the  $\alpha$ -position is blocked with a methyl group, bromination under all conditions gives only a single substance. Thus, no isomers could be obtained by brominating the substances represented by the formulas,

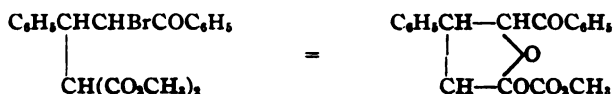


Very closely related substances, on the other hand, on bromination under the same conditions, invariably give stereo-isomeric  $\gamma$ -bromo compounds. This is true, for example, of the series,<sup>6</sup>



In view of these conflicting analogies it became desirable to determine the structure of the bromine derivatives of the malonic esters beyond question. All attempts to accomplish this by replacing the halogen with other groups failed, owing to the ease with which the isomers lose hydrogen bromide. Of the many reagents tried, potassium thiocyanate alone in part replaces the bromine. Unfortunately the structure of the resulting thiocyanate is no easier to determine than that of the bromine compounds themselves.

The principal difference between the 2 bromine compounds is in their behavior on heating. When the lower-melting isomer is heated under greatly reduced pressure it begins to evolve gas at about 125°, and above 150° it decomposes freely. The residue left, after the evolution of gas ceases, consists largely of a ketolactonic ester whose structure was established with certainty. The reaction by which this is formed is represented by the equation,

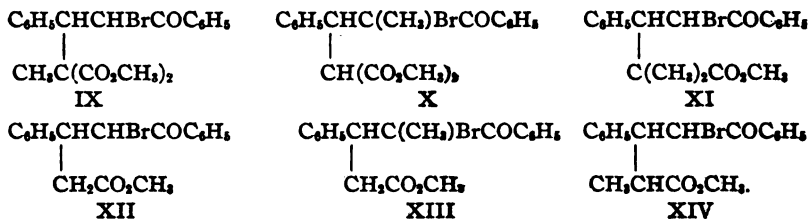


The low-melting bromine compound must, therefore, be a  $\gamma$ -bromo derivative.

<sup>6</sup> Ref. 2, p. 1411.

<sup>6</sup> THIS JOURNAL, 38, 889 (1916).

The higher-melting bromine compound is much more stable. It does not decompose perceptibly below  $200^{\circ}$  and most of it can be recovered after it has been heated for hours at  $225^{\circ}$ . The products of decomposition at this high temperature indicate deep seated changes. The substance, therefore, is probably not a  $\gamma$ -bromo compound. The evidence, however, is not conclusive, for while the  $\gamma$ -bromo compounds represented by Formulas IX–XI lose methyl bromide on heating, those represented by XII–XIV do not.



The process evidently depends upon the ease of ring formation and this, as is known, is affected by configuration as well as structure.

The matter was finally cleared up by the discovery of a third monobromo derivative. When the lower-melting isomer ( $102^{\circ}$ )<sup>7</sup> is heated with bromine in chloroform it gives in addition to one of the dibromo compounds previously described (m. p.  $132^{\circ}$ ) a small quantity of an isomeric compound melting at  $120^{\circ}$ . The structure of these two substances is, doubtless, different, for while the former gives nothing but the cyclopropane derivative when it is boiled with alcoholic potassium iodide,<sup>8</sup> the latter on similar treatment is reduced, first to a new monobromo derivative, and finally to the ketonic ester.

The monobromo compound (m. p.  $77^{\circ}$ ) is different from either of those previously described. Like them it gives a mixture of isomeric cyclopropane derivatives when boiled with methyl alcoholic potassium acetate, and therefore is either an  $\alpha$ - or a  $\gamma$ -bromo compound. When heated under diminished pressure it behaves exactly like the isomer that melts at  $102^{\circ}$ , losing methyl bromide rapidly at  $150^{\circ}$  and passing into the same ketolactonic ester. These two substances are consequently the  $\gamma$ -bromo compounds represented by Formula I. and the isomer that melts at  $113^{\circ}$  must be an  $\alpha$ -bromo derivative.

The behavior of these  $\gamma$ -ketonic esters towards bromine may therefore be summed up as follows. In methyl alcohol the sole product is one of the 2 possible stereo-isomeric  $\gamma$ -bromo compounds. In chloroform or carbon tetrachloride bromination gives a mixture of approximately equal amounts of  $\alpha$ - and  $\gamma$ -bromo compounds. Since the reaction stops sharply with the replacement of one hydrogen atom it follows that a bromine

<sup>7</sup> The melting point previously given for this substance was  $98^{\circ}$ . Ref. 2, p. 1411.

<sup>8</sup> Ref. 2, p. 1413.

atom in either of these positions interferes with the introduction of bromine in the other one.

### Experiments

#### 1. Addition of Methyl Dimethylmalonate to Unsaturated Ketones.

—Alkyl malonic esters do not combine nearly so readily as the unsubstituted esters with  $\alpha,\beta$  unsaturated ketones. Inasmuch, however, as the addition products neither are capable of combining with a second molecule of unsaturated ketone to form dimolecular products nor are easily hydrolyzed to the corresponding acids it is possible to use larger amounts of condensing agent and still secure excellent yields. The procedure adopted in all cases was as follows. A solution of sodium methylate containing 1 g. of sodium in the minimal quantity of dry methyl alcohol was added to a hot conc. solution of equivalent quantities of the ester and ketone. The mixture<sup>1</sup> was boiled for an hour and then allowed to cool very slowly. Most of the addition product separated in almost pure condition. The remainder, somewhat less pure, was obtained by acidifying and evaporating the filtrates. The products were purified by recrystallization from methyl alcohol. The yields were excellent, generally exceeding 95%.

**Methyl  $\beta$ -phenyl- $\gamma$ -benzoyl-ethylmethylmalonate**, (Formula III).—The addition product obtained with benzal-acetophenone crystallizes in needles, is moderately soluble in all the common organic solvents except petroleum ether, and melts at 121–122°.

*Analysis.* Calc. for  $C_{21}H_{22}O_6$ : C, 71.2; H, 6.2. Found: C, 71.1; H, 6.4.

**Methyl  $\beta$ -phenyl- $\gamma$ -(4-bromobenzoyl)-ethylmethylmalonate**, crystallizes in aggregates of fine needles less soluble in organic solvents than the corresponding bromine-free compound. It melts at 89°.

*Analysis.* Calc. for  $C_{21}H_{21}O_6Br$ : C, 58.2; H, 4.8. Found: C, 57.9; H, 5.0.

**Methyl  $\beta$ -phenyl- $\gamma$ -(4-methoxybenzoyl)-ethylmethylmalonate**, (Formula V).—The product obtained by adding methyl dimethylmalonate to benzal-*p*-methoxyacetophenone crystallizes in fine needles and melts at 120–122°.

*Analysis.* Calc. for  $C_{22}H_{24}O_6$ : C, 68.7; H, 6.6. Found: C, 68.3; H, 6.6.

#### Bromination of the Methylmalonic Ester Addition Products

Two methods for introducing bromine into malonic ester addition products were described in an earlier paper.<sup>9</sup> The common method of brominating in a solvent in which hydrogen bromide is sparingly soluble goes rapidly and completely in the cold, stops sharply with the introduction of one bromine atom and gives a mixture of two isomeric substitution products. Bromination in methyl alcohol or better in methyl alcohol previously saturated with hydrogen bromide proceeds slowly in the sunlight, requires excess of bromine and even then is incomplete, but invariably gives only a single bromine compound. Both of these methods were tried with each of the foregoing compounds, the first at the temperature of a freezing mixture as well as at the boiling point of carbon tetra-

<sup>9</sup> Ref. 2, p. 1411.

chloride. Each substance under all conditions gave only a single monobromo derivative. The bromo compounds were purified by recrystallization from methyl alcohol.

**Methyl  $\beta$ -phenyl- $\gamma$ -bromo- $\gamma$ -benzoyl-ethylmethylnmalonate, (Formula IX).**—The substance is sparingly soluble in ether, moderately in methyl alcohol and in carbon tetrachloride, and very readily soluble in chloroform. It crystallizes in stout needles or prisms, melts at 156–157°, and when the temperature is raised rapidly it begins to decompose at about 190°.

*Analysis.* Calc. for  $C_{21}H_{21}O_4Br$ : C, 58.2; H, 4.8. Found: C, 58.0; H, 4.9.

**Methyl  $\beta$ -phenyl- $\gamma$ -bromo- $\gamma$ -(4-bromophenyl)-ethylmethylnmalonate.**—The single bromo compound obtained by brominating the corresponding ester, crystallizes in needles, melts at 140°, and when the temperature is raised rapidly, begins to decompose at about 90°.

*Analysis.* Calc. for  $C_{21}H_{19}O_4Br_2$ : C, 49.2; H, 3.9. Found: C, 49.2; H, 4.0.

**Methyl  $\beta$ -phenyl- $\gamma$ -bromo- $\gamma$ -(4-methoxybenzoyl)-ethylmethylnmalonate.**—The ester melting at 122° gave under all conditions a single bromo compound which crystallized in needles, melted at 151° and when heated rapidly began to decompose at about 190°.

*Analysis.* Calc. for  $C_{22}H_{23}O_5Br$ : C, 57.0; H, 5.0. Found: C, 56.7; H, 5.3.

**Replacement of Bromine in the Monobromo Compounds.**—With a view to replacing the halogen with other groups and thus getting substances that could be manipulated without fear of obtaining cyclopropane compounds, the 2 isomeric monobromo derivatives of benzoyl-phenyl-ethylmalonate were treated with amines, cyanides, silver nitrite, silver acetate, alcoholates, and potassium thiocyanate. All of these, except the thiocyanate, gave under all conditions by which they could be induced to react either a cyclopropane derivative or secondary products formed from the cyclopropane derivative. When the lower-melting isomer (98°) was digested for several hours with potassium thiocyanate in dry methyl alcohol, it gave a mixture of the 2 isomeric cyclopropane derivatives (90%) and a thiocyanate (10%). The mixture was separated by fractional crystallization from a mixture of ether and methyl alcohol. The thiocyanate crystallizes in colorless needles, is moderately soluble in common organic solvents and melts at 133°.

*Analysis.* Calc. for  $C_{21}H_{19}O_4SN$ : C, 63.5; H, 5.0. Found: C, 63.8; H, 5.1.

The higher-melting isomer also gave a mixture of cyclopropane derivatives and a sulfur compound, but the yield of the latter was so small and its isolation so difficult that a complete separation of the mixture was not attempted.

### Preparation of a Third Isomeric Bromo Compound

All methods of direct bromination gave only 2 of the 3 possible monobromo substitution products of methyl-phenyl-benzoyl-ethylmalonate; but there still remained the possibility that the third might result from reduction of a more highly brominated derivative. As was shown in an earlier paper<sup>10</sup> both of the monobromo compounds on further bromination give two solid  $\alpha,\gamma$ -dibromo derivatives (112° and 94°) along with considerable quantities of oily products. These solid products were reduced with zinc and alcohol, zinc and acetic acid and also catalytically using

<sup>10</sup> Ref. 1, p. 484.

colloidal palladium; but it was found impossible to control the process. The result was always the cyclopropane, the bromine-free ketonic ester or, more frequently, a mixture of the two. This was doubtless due to the fact that the first step in each case was the removal of the 2 bromine atoms and the formation of the cyclopropane derivative. Attention was therefore directed to the oil obtained in brominating the lower-melting isomer (98°). By allowing a solution of this in a mixture of ether and petroleum ether to evaporate very slowly a third solid was obtained in small quantities. This proved to be a  $\gamma,\gamma$ -dibromo derivative.

**Methyl  $\beta$ -phenyl- $\gamma,\gamma$ -dibromo- $\gamma$ -benzoyl-ethylmalonate,  $C_6H_5CHCBr_2COC_6H_5$ .**  
 $\quad \quad \quad |$   
 $\quad \quad \quad CH(CO_2CH_3)_2$

The third solid obtained by brominating the lower-melting monobromo compound, crystallized in plates and melted at 126°.

**Analysis.** Calc. for  $C_{10}H_{18}O_5Br_2$ : C, 48.2; H, 3.6. Found: C, 47.9; H, 3.8.

That this is neither an  $\alpha, \gamma$  nor a  $\beta, \gamma$  derivative is shown by its behavior towards potassium iodide. When the  $\alpha, \gamma$ -dibromo compounds are boiled with a methyl alcoholic solution of this reagent they lose bromine rapidly and pass into cyclopropane derivatives.<sup>11</sup> Dibromo compounds which have bromine in the  $\alpha, \beta$  positions to carbonyl likewise lose bromine very rapidly when they are boiled with alcoholic solutions of potassium iodide, the product being an unsaturated ketone. The dibromo compound in question does not behave like either of these types. In the absence of free acid it is scarcely affected by potassium iodide. In the presence of acetic acid it is slowly reduced giving first a monobromo derivative and finally the saturated ketonic ester. It must, therefore, be the  $\gamma, \gamma$ -dibromo compound.

**Methyl  $\beta$ -phenyl- $\gamma$ -bromo- $\gamma$ -benzoyl-ethylmalonate** (Formula I).—A methyl alcoholic solution of 25 g. of the  $\gamma,\gamma$ -dibromo compound, 10 g. of potassium iodide and about 0.5 g. of acetic acid were boiled for 4 hours, then concentrated by distilling most of the methyl alcohol and poured into an aqueous solution of sodium hydrogen sulfite. From these organic compounds were extracted with ether. The ethereal solution was thoroughly washed with water and sodium carbonate, dried over calcium chloride, concentrated, and diluted with petroleum ether. That at once precipitated a small quantity of unchanged dibromo compound. The filtrate from the dibromo compound on slow evaporation deposited a mixture of needles and plates which was separated mechanically. The needles, after recrystallization from methyl alcohol, melted at  $105^\circ$  and were identified as phenyl-benzoyl-ethylmalonate. The plates after several recrystallizations from a mixture of ether and petroleum ether melted at  $76-77^\circ$ .

**Analysis.** Calc. for  $C_{10}H_{11}O_2Br$ : C, 57.3; H, 4.5. Found: C, 57.0; H, 4.6.

The new monobromo compound behaves toward reagents exactly like the two previously known. When heated with potassium acetate, it loses hydrogen bromide and gives mainly the cyclopropane derivative melting at 72°.

**Behavior of the Three Isomeric Monobromo Compounds when Heated.**—Twenty g. of the bromo compound melting at 102° was heated under atmospheric pressure in a distilling flask which was immersed in a metal bath. The volatile products were passed into a brine solution which was cooled in a freezing mixture. Decomposition commenced when the temperature of the bath reached about 190° and was complete after 2 hours' heating at 190–200°. The volatile products were hydrogen bromide, free

<sup>11</sup> Ref. 2, p. 1413.

bromine, and methyl bromide which collected as a liquid under the brine and was identified by the boiling point.

The pale yellow residue left in the flask partially solidified when rubbed with methyl alcohol. The solid after recrystallization melted at  $106^{\circ}$  and was identified as methyl phenyl-benzoyl-ethylmalonate. The filtrate from this contained a mixture of substances including about 8 g. of a new substance which melted at  $93^{\circ}$ . At this high temperature the decomposition evidently proceeds in two directions, one resulting in the loss of hydrogen bromide which reduces a part of the bromo compound to the ketonic ester, the other giving methyl bromide and the compound melting at  $93^{\circ}$ .

When the heating is conducted under greatly diminished pressure, the process is much cleaner. Heated under 8 mm. in contact with porous plate, the bromo compound begins to decompose at about  $150^{\circ}$  and the evolution of gas continues at a fair speed even when the temperature is subsequently lowered to  $125^{\circ}$ . Under these conditions the yield of the product melting at  $93^{\circ}$  exceeds 80%.

**Methylphenyl-benzoyl-butyrolactone-carboxylate.**—The substance which melts at  $93^{\circ}$  is readily soluble in the common organic solvents except petroleum ether. From methyl alcohol it separates in fine needles which slowly change to stout needles or prisms if allowed to remain in contact with the mother liquor.

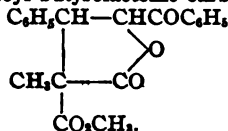
*Analysis.* Calc. for  $C_{18}H_{16}O_6$ : C, 70.4; H, 5.0. Found: C, 70.2; H, 5.1.

Although there could be little question as to the nature of this substance, it was deemed worth while to make it by a method that leaves no doubt as to its structure. For this purpose a methyl alcoholic solution of the ketonic ester was treated with the amount of potassium hydroxide calculated to hydrolyze only one of its ester groups. This solution became neutral in the course of several hours. An equivalent amount of bromine was then added. This disappeared slowly at the ordinary temperature and the resulting colorless solution, on evaporation, deposited almost the calculated quantity of the substance melting at  $93^{\circ}$ . It is therefore a  $\gamma$ -lactonic ester, and the bromine compound melting at  $76^{\circ}$  must be a  $\gamma$ -bromo derivative.

The Isomeric Bromine Compound melting at  $77^{\circ}$ , when heated under diminished pressure, began to decompose at about  $150^{\circ}$  and continued to effervesce freely when the temperature was lowered to  $130^{\circ}$ . The yellow melt left after heating for 2 hours gave mainly the ketolactonic ester which melts at  $93^{\circ}$ . This isomer is, therefore, likewise a  $\gamma$ -bromo compound.

The Isomer which Melts at  $113^{\circ}$  must be the  $\alpha$ -bromo derivative. When it was heated under diminished pressure it began to decompose slowly at about  $200^{\circ}$ . From the dark melt left after 2 hours' heating at  $200$ – $225^{\circ}$  more than half of the bromo compound was recovered. The only other substance isolated was the bromine-free ketonic ester. The volatile products were, in part, condensed in a receiver that was cooled in solid carbon dioxide and ether. They were composed mainly of hydrogen bromide, bromine, malonic ester, and a small quantity of benzal-acetophenone dibromide.

**Methylmethyl-phenyl-benzoyl-butyrolactonic-carboxylate:**



The  $\gamma$ -bromo compounds of the ketonic esters that are obtained by adding esters of methyl malonic acid to unsaturated ketones, lose methyl bromide rapidly at comparatively low temperatures. The yield of lactonic ester obtained by heating the bromo compound represented by the formula IX was nearly 90%. The substance crystallizes in needles and melts at  $108^{\circ}$ .

*Analysis.* Calc. for  $C_{20}H_{18}O_6$ : C, 71.0; H, 5.3. Found: C, 71.1; H, 5.5.

### Summary

1. When ketonic esters, which have a malonic ester residue in the  $\beta$ -position to the carbonyl group, are brominated in methyl alcohol, the only product is a monobromo compound which has bromine  $\alpha$  to carbonyl.

2. When the same esters are brominated in chloroform or carbon tetrachloride, the result is a mixture of monobromo derivatives. In one of these the bromine is  $\alpha$  to carbonyl, in the other it is in the malonic ester residue.

3. A third monobromo derivative was obtained by first introducing two bromine atoms  $\alpha$  to carbonyl and then replacing one of these with hydrogen.

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[CONTRIBUTION FROM THE DEPARTMENT OF PHARMACOLOGY, HARVARD MEDICAL SCHOOL.]

## THE SULFUR CONTENT OF ARSPHENAMINE AND ITS RELATION TO THE MODE OF SYNTHESIS AND THE TOXICITY. I<sup>1</sup>

BY WALTER G. CHRISTIANSEN

Received January 17, 1922

In the course of an investigation designed to bring out any existing relation between the sulfur content and the toxicity of arsphenamine, a large number of samples were prepared by hydrosulfite reduction of 3-nitro-4-hydroxyphenylarsonic acid using the same quantities of reagents, but reducing the nitro group under varying conditions.<sup>2</sup> Thus a series of specimens was obtained in which the toxicity, as determined by intravenous injection into white rats, varied from 50 to 150 mg./kg. The results are given in the accompanying graph (Fig. 1).

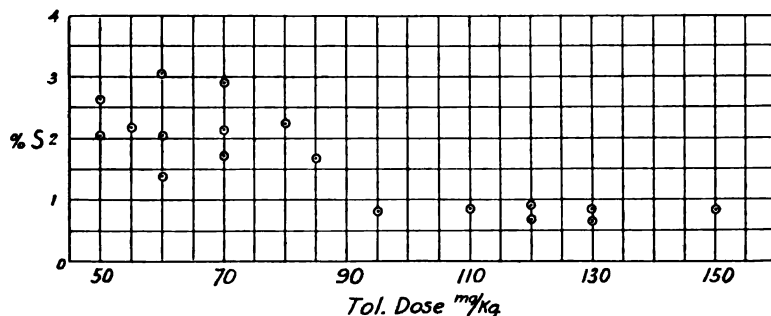


Fig. 1.—Sulfur content and tolerated dose of arsphenamine.

<sup>1</sup> This is the sixth of a series of studies on the properties contributing to the toxicity of arsphenamine being made under a grant from the United States Interdepartmental Social Hygiene Board to the Harvard Medical School; the work is under the general direction of Dr. Reid Hunt, who is also responsible for the biological tests reported in this paper.

<sup>2</sup> The conditions affecting the toxicity were discussed in *THIS JOURNAL*, 43, 2202 (1921).



Although there is no direct relation between the toxicity and the total sulfur content, it is evident that the least toxic preparations have less than 1% of sulfur and the most toxic contain 1.5–3.0%. Inasmuch as 7 samples containing 0.66 to 0.94% of sulfur were tolerated in doses varying from 95 to 150 mg./kg., and 5 containing 2.04 to 2.25% of sulfur had tolerated doses varying from 50 to 80, and 3 which were tolerated at 60 mg. contained 1.40, 2.09, and 3.03% of sulfur, it follows that either the toxicity is only partly due to the presence of toxic sulfur compounds or the sulfur can be present in more than one state of combination and affects the toxicity differently when in different combinations. These results also prove that the extent to which sulfur compounds are formed depends upon the manner in which the nitro group is reduced.

This bears a striking resemblance to the relation found between the mode of reduction of the nitro group and the toxicity. Methods were developed for the production of relatively toxic and non-toxic arspenamine from the nitro acid, and it was proved that the consistent production of the least toxic material required the use of the corresponding pure amino acid as starting material.<sup>2</sup> Upon analysis it was found that the sulfur content is lowest in material obtained from the amino acid,<sup>3</sup> slightly higher when the nitro acid is reduced under the conditions favoring the lowest toxicity, and much higher when the reverse conditions are used (Table I).

TABLE I

## THE MODE OF SYNTHESIS, TOXICITY AND SULFUR CONTENT OF ARSPENAMINE

Arspenamine prepared by hydrosulfite reduction of	Expt.	Average	Limit of	Average S content %	Limit of S content %
		tolerated dose Mg./kg.	tolerated dose Mg./kg.		
Amino acid.....	2	145	140–150	0.43	0.41–0.46
Nitro acid I.....	3	137	130–150	0.80	0.66–0.87
Nitro acid II.....	7	62	50–85	2.08	1.40–3.03

Since high toxicity produced in this way is concomitant with high sulfur content the nature of the sulfur compounds present and their relation to the toxicity were taken under consideration.

It is only the sulfur compounds resulting from phenomena occurring during the reduction of the nitro group which may cause the excessive toxicity of these products. Since the mechanism of the reaction, after the nitro group is reduced is the same as in the reduction of amino acid, an amount of sulfur equal to that found in arspenamine prepared from amino acid will be introduced during this part of the synthesis. Therefore, the sulfur content of arspenamine prepared from the amino acid may be subtracted from that of material made from the nitro acid and we find that arspenamine made from the nitro acid contains 0.37 or

<sup>3</sup> This agrees with the observation made by Fargher and Pyman, *J. Chem. Soc.*, 117, 370 (1920).

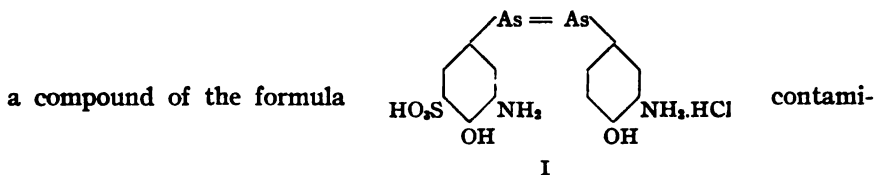
1.65% sulfur which is introduced during the reduction of the nitro group, depending upon the set of conditions used. Evidently when the nitro group is reduced under the most favorable conditions, very little sulfur enters the molecule.

Arsphenamine sulfate is present but can be formed as readily during the reduction of the amino acid as during the reduction of the nitro acid and is probably present in all samples to about the same extent.<sup>4</sup> Moreover, as the sulfate and hydrochloride prepared from the same base have equal toxicities, the formation of this substance could have no effect on the toxicity. Since it is formed after the nitro group has been reduced, it contributes its sulfur to that subtracted from the total sulfur in order to obtain the figure representing the sulfur introduced when the nitro group is reduced.

It has been suggested,<sup>5</sup> but not demonstrated, that sulfur compounds in which the sulfur is attached to the arsenic atom may be present. These substances, if present, would be formed during the reduction of the arsonic acid group, *i. e.*, after the nitro group has been reduced and they should constitute a fairly constant part of the total sulfur in arsphenamine prepared either from the amino acid or from the nitro acid. This, then, is also part of the sulfur subtracted from the total sulfur of arsphenamine made from the nitro acid.

Since arsphenamine prepared by hydrosulfite or hypophosphorous acid reduction of the pure amino acid has the same low toxicity, the sulfur introduced during hydrosulfite reduction can have no bearing upon the toxicity.

In the work of Fargher and Pyman<sup>6</sup> and later of King<sup>7</sup> sulfur compounds present as impurities in arsphenamine are discussed. The former investigators showed that a conc. methyl alcohol solution of arsphenamine, prepared by reduction of the nitro acid, deposited a precipitate which had a high sulfur content. A methyl alcohol solution of arsphenamine prepared from the amino acid deposited very little material on standing. Thus, the compound containing the sulfur introduced during the nitro group reduction could be separated. At first the precipitate was thought to be a sulfamic acid, but King subsequently showed that it was mainly



<sup>4</sup> Except when the hydrochloride is precipitated from aqueous solution by conc. hydrochloric acid.

<sup>5</sup> Fargher and Pyman, Ref. 3.

<sup>6</sup> King, *J. Chem. Soc.*, 120, 1107, 1414 (1921).

nated by a little arsphenamine sulfate. It is probable that the small quantities of solid which Fargher and Pyman obtained from solutions of the arsphenamine prepared from the amino acid consisted of arsphenamine sulfate. King states that (I) is the main sulfur impurity in arsphenamine and being more toxic than the latter is an undesirable impurity.

If this sulfonic acid derivative is the main sulfur impurity in arsphenamine, it would be possible, by allowing a conc. methyl alcohol solution to stand, to obtain from the mother liquor, after removal of the precipitate, arsphenamine with a sulfur content nearly as low as that found when the pure amino acid is used as a source of arsphenamine, *i. e.*, 0.43%. The difference between 0.43 and the sulfur found would be due to the solubility of the sulfonic acid. By reducing mixtures of 3-amino-4-hydroxyphenylarsonic acid and its 5-sulfonic acid,<sup>6</sup> arsphenamines of varying sulfur content were prepared in which the main sulfur impurity was necessarily the sulfonic acid (I). A solution of 1 g. in 4 cc. of absolute methyl alcohol was allowed to stand for 20 to 24 hours in the absence of air and moisture and then was centrifuged. The solid was washed once with methyl alcohol; the mother liquor and washing were united and poured into ether to precipitate the material which had remained in the alcoholic solution.

TABLE II  
REMOVAL OF THE SULFONIC ACID DERIVATIVE BY FRACTIONATION IN METHYL ALCOHOL

Ratio of amino acid to amino-sulfonic acid used for reduction	Reduction Product		CH <sub>3</sub> OH soluble part
	Tol. dose Mg./kg.	% S	% S
4.1 : 1	90	1.75	0.69
4.1 : 1	ca. 80	2.10	0.80
8.6 : 1	90	1.50	1.08
8.6 : 1	ca. 80	1.23	0.98
12 : 1	110 or above	0.99	0.77
12 : 1	100	1.03	..
17 : 1	ca. 90	0.95	0.79
			Av. 0.85

These results (Table II) show that arsphenamine so prepared that the main sulfur impurity is the sulfonic acid derivative will deposit this impurity from a methyl alcohol solution in varying degrees depending upon the degree of contamination and that the material which remains in solution has a fairly constant sulfur content, 0.85%. In the last experiment the precipitation was very slight, and since the original sulfur content, 0.95%, is only slightly higher than the average sulfur of the material recovered from the mother liquor, arsphenamine containing less sulfonic acid than this would not deposit a solid under the conditions used. When methyl

alcohol solutions of arspenamine prepared from the nitro acid by the two methods previously developed were treated as above, it was found that the low sulfur-containing (0.83, 0.58%), slightly toxic, specimens gave no insoluble matter. This would be expected from the fact that the sulfur content is below that found in the above alcohol-soluble material. However, upon similar examination of the high sulfur-containing, highly toxic samples, a precipitate insoluble in methyl alcohol was obtained, but the sulfur contents were lowered from 2.09, 1.64 and 1.75% to only 1.49, 1.13 and 1.31% respectively. Again, the sulfur content of the alcohol-soluble material is fairly constant, averaging 1.31%, but is considerably higher than that found for specimens to which a known amount of the sulfonic acid had been added. The difference between 0.85 and 1.31, *i. e.*, 0.46, is the average percentage of sulfur in high sulfur-containing arspenamine which is introduced during the reduction of the nitro group but which cannot be removed from concentrated methyl alcohol solution as sulfonic acid.

In King's work these experiments were carried out using 1 g. of arspenamine to 3 cc. of methyl alcohol, but in order to facilitate the preparation of the solutions, 4 cc. of alcohol was used in the work here reported. This might introduce a slight variation in the absolute sulfur content but would not affect the difference noted between the two sets of experiments. To determine the extent to which differences in concentration affected the results, 1 g. of arspenamine produced by reducing a mixture of 1.4 parts of amino acid and 1 part of the sulfonic acid was treated with 4 cc. of methyl alcohol in one case and 10 cc. in another. The original sulfur content was 2.10% and that of the material recovered from the alcoholic mother liquor 0.80 and 1.21% in the respective experiments. Evidently, the difference between using 3 cc. and 4 cc. of methyl alcohol would be very slight.

In the preceding table (II) it appears that reduction of mixtures of the amino acid and its 5-sulfonic acid gives products which are more toxic than arspenamine obtained from the pure amino acid, but instead of having a direct relation between the amount of sulfonic acid added and the toxicity all the samples have approximately the same tolerated dose. This may indicate that the increased toxicity is not due directly to the presence of the sulfonic acid compound but the presence of the latter substance may cause variations in the properties (colloidal) of arspenamine, thus acting indirectly; a small quantity present during the synthesis might be sufficient to effect such a change. The amino acid used in the above experiments gave, when reduced by itself, a product of low toxicity.

When the nitro acid is reduced under the most favorable conditions, the arspenamine has on an average 0.80% of sulfur and a tolerated dose

of 137 mg./kg. indicating that 0.37% of sulfur is introduced during the reduction of the nitro group. Even the presence of only enough sulfonic acid to cause arsphenamine made from the amino acid to have a sulfur content of 0.95% instead of the customary 0.43% results in a decrease in tolerated dose to about 90 mg./kg.; consequently the 0.37% of sulfur introduced with the nitro group cannot have entered the molecule in a sulfonic acid group.

It was proved above that the high sulfur arsphenamines contain on an average 0.46% of sulfur which is introduced during the reduction of the nitro group but which cannot be removed from conc. methyl alcohol solution as sulfonic acid, and it now appears that 0.37% of sulfur is introduced under the most favorable conditions for reduction of the nitro group, does not enter the molecule as sulfonic acid and does not materially alter the toxicity. These figures agree well within the experimental error, and it is entirely probable that this amount of sulfur will enter the molecule in this form no matter how the nitro group is reduced.

It is now possible to state in what form the sulfur is present in arsphenamine, the extent of each form, and its relation to the toxicity if the method of preparation is known (Table III).

TABLE III  
DISTRIBUTION OF SULFUR IN ARSPHENAMINE

Source of Arsphenamine	S Content %	Remarks
(a) Pure Amino Acid	0.43	Arsphenamine sulfate and possibly arsenic-sulfur compounds; no effect on toxicity.
(b) Nitro Acid I	0.43	Present as in (a).
	0.37	Introduced as a result of reduction of the nitro group; not present as sulfonic acid group; little effect on toxicity.
	— 0.80	
(c) Nitro Acid II	0.43	
	0.37-0.46	
	— 0.80-0.89	Present as in (b).
Total S less above (Av. 0.85) = 1.23 (Av.)		Introduced as a result of reduction of nitro group, removable as sulfonic acid; very closely related to the toxicity.

Therefore, in high sulfur arsphenamine obtained by reduction of the nitro acid approximately 20% of the total sulfur is not a result of the reduction of the nitro group; 20% is a result of this reduction but does not affect the toxicity; while 60% results from this reduction, is closely related to the toxicity and could, if the 5-sulfonic acid derivative of ars-

phenamine were completely insoluble in methyl alcohol, be removed as such.

Fargher and Pyman<sup>7</sup> calculated from chlorine values and neutralization values the amount of sulfur present in arspenamine as sulfamic acid; this, according to King,<sup>6</sup> is present as sulfonic acid. In 10 commercial samples the average total sulfur was 1.50% (1.26–1.77%) and calculation showed 0.75% (0.27–1.37%) of sulfur as 'sulfamic acid'; therefore their figures show an average of 50% of the total sulfur present as 'sulfamic' acid. This figure agrees well with the average value (60%) calculated above for the sulfur introduced by improper reduction of the nitro group and separable as sulfonic acid.

A comparison of the toxicity which it is possible to obtain by reduction of the nitro acid (62 mg./kg., varying between 50 and 85) with the toxicity of products obtained by reducing mixtures of the amino acid and its sulfonic acid (about 90 mg./kg.), shows that the presence of the sulfonic acid derivative of arspenamine can account for only part of the toxicity which is found.

The sulfur determinations were made by carbonate-peroxide fusion;<sup>1</sup> after addition of the barium chloride the solution was evaporated to 150–200 cc. and allowed to stand 40–48 hours before filtration. Owing to the low sulfur content and the fact that it was seldom possible to use over 0.3 g. of substance for each analysis, the barium sulfate obtained was always less than 60 mg. and averaged 30 mg. The solution from which this is obtained contains a large quantity of inorganic salts, about 17 g. of sodium chloride being the main one. To determine the effect of this upon the weight of the barium sulfate, weighed amounts of carefully purified potassium sulfate were fused and analyzed by the above procedure. The following 8 determinations (Table IV) were made; to eliminate any personal factor they were made by two investigators.

TABLE IV  
ANALYSES OF POTASSIUM SULFATE

K <sub>2</sub> SO <sub>4</sub> taken	BaSO <sub>4</sub> found	BaSO <sub>4</sub> calc.	Diff.
Mg.	Mg.	Mg.	Mg.
6.3	13.5	8.4	5.1
9.2	16.8	12.2	4.6
11.7	20.3	15.7	4.6
16.6	26.6	22.2	4.4
18.8	30.5	25.2	5.3
24.6	37.2	32.9	4.3
27.1	40.4	36.3	4.1
29.9	44.4	40.1	4.3
			—
			4.6

In this method of analysis there is a constant error which causes the barium sulfate found to be 4.6 mg. too high and this correction must be applied.

In preparing arspenamine intentionally contaminated by sulfonic acid the mixture of the amino acid and its sulfonic acid was reduced by the method used for the pure amino acid. The base after drying *in vacuo* was treated with methyl-alcoholic hydrochloric acid and this solution,

<sup>7</sup> Meyer, "Analyse Organischer Verbindungen," J. Springer, 1909, p. 223.

except in cases where the amount of sulfonic acid was very high, could be filtered without the sulfonic acid separating. The material was precipitated by ether in the usual way.

### Summary

1. A careful study of the mode of synthesis, toxicity and sulfur content shows that arspenamine prepared (a) from the amino acid is the least toxic and has the lowest sulfur content; (b) from the nitro acid under the most favorable conditions is slightly more toxic and has a slightly higher sulfur content; (c) from the nitro acid under least favorable conditions is much more toxic and has a much higher sulfur content.
2. There is no direct relation between the total sulfur and the toxicity.
3. Only the sulfur in excess of that introduced when the nitro acid is reduced under the most favorable conditions has any great effect upon the toxicity.
4. Only from those preparations made from the nitro acid under the least favorable conditions can the sulfonic acid derivative of arspenamine described by King be isolated, and the amount which the sulfur content can be lowered by removal of this substance is nearly the same as the excess sulfur introduced by improper reduction of the nitro group.
5. The presence of this sulfonic acid derivative cannot account for the whole of the high toxicity which is obtainable.

I wish to express my appreciation of Dr. Reid Hunt's work in determining the toxicity of the substances used in this paper, and of Mr. Arthur J. Norton's assistance in determining the correction to be applied in the sulfur analyses.

BOSTON, MASSACHUSETTS

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[CONTRIBUTION FROM THE DEPARTMENT OF PHARMACOLOGY, HARVARD MEDICAL SCHOOL]  
**THE SULFUR CONTENT OF ARSPHENAMINE AND ITS RELATION  
TO THE MODE OF SYNTHESIS AND THE TOXICITY. II<sup>1</sup>**

By WALTER G. CHRISTIANSEN

Received January 17, 1922

While comparing high sulfur-containing, highly toxic arspenamine obtained by the hydrosulfite reduction of 3-nitro-4-hydroxyphenylarsonic acid<sup>2</sup> with high sulfur-containing samples<sup>3</sup> prepared from known mixtures

<sup>1</sup> This is the seventh of a series of studies on the properties contributing to the toxicity of arspenamine being made under a grant from the United States Interdepartmental Social Hygiene Board to the Harvard Medical School; the work is under the general direction of Dr. Reid Hunt who is also responsible for the biological tests reported in this paper.

<sup>2</sup> This type of arspenamine will be referred to as arspenamine I; for preparation, see *THIS JOURNAL*, 43, 2202 (1921).

<sup>3</sup> Arspenamine II; for preparation, see preceding paper.

of 3-amino-4-hydroxyphenylarsonic acid and its 5-sulfonic acid,<sup>4</sup> it was found that although both deposit the 5-sulfonic acid derivative of arspenamine from a conc. methyl alcohol solution there are several points of difference between the two types of preparations. Some of these are the rate at which the sulfonic acid separates from the alcohol solution, the effect of temperature on the formation of the precipitate, the ease of separation of the precipitate from the mother liquor and the rate of death of rats when the substances are injected intravenously.

Fargher and Pyman<sup>5</sup> and later King,<sup>4</sup> working with English commercial samples, reported that the solid separates only slowly from alcoholic solution. This observation was found to be true, many solutions of high sulfur arspenamine showing no signs of turbidity for a number of hours. When variations in the temperature were made marked changes were produced in the rate of precipitation. In the experiments on arspenamine I recorded in the following table the alcoholic solutions were made at 0° and kept in completely filled stoppered tubes.

TABLE I  
PRECIPITATION OF ARSPHENAMINE I FROM ALCOHOLIC SOLUTION

Ratio of Arsph. to S		Temp.	Time in hours						Effect of warming to 45°
CH <sub>3</sub> OH	Content		1/2	1	2	4	20	45	
G.:Cc.	%	° C.							
1:5	1.40	0	0	0	0	0	0	0	
1:4	1.56	0	0	0	0	0	0	0	
1:4	1.73	0	0	0	0	0	0	—	++in 20 min.
1:4	1.87	0	0	0	0	0	+		
1:3	..	0	0	0	0	0	+	+++	
1:4	1.47	8	0	0	0	0	+		+++in 15 min.
1:5	1.40	23	0	0	0	0	+++		
1:4	1.87	R.T.*	0	0	0	—	+++		
1:3	1.64	R.T.	0	0	+	++	+++		
1:3	..	R.T.	0	+	++	+++			
1:5	2.04	45	+	+++					
1:5	1.40	45	0	+	+++				
1:3	..	45	+++						

+ Turbid.

++ Slight precipitate.

+++ Heavy precipitate.

\* Room temperature.

These results show that at any one temperature precipitation is more rapid from a concentrated than from a dilute solution, and that at any one concentration precipitation becomes faster as the temperature is raised. Temperature has the greater effect as a 1:5 solution at 23° or 45° separated faster than a 1:3 solution at 0° or room temperature respectively. Also,

<sup>4</sup> King, *J. Chem. Soc.*, 120, 1107 (1921).

<sup>5</sup> Fargher and Pyman, *ibid.*, 117, 370 (1921).



the immediate precipitation caused by warming a solution which has only undergone a slight change at 0° shows the importance of the temperature.

A similar series of experiments (Table II) was run with arsphenamine II, *i. e.*, arsphenamine whose main sulfur impurity is necessarily the 5-sulfonic acid derivative in varying amounts.

TABLE II  
PRECIPITATION OF ARSPHENAMINE II FROM ALCOHOLIC SOLUTION

Ratio of Arsph. to CH <sub>3</sub> OH		S Content	Temp.	Time in hours					Warm to 45°
G.:Cc.	%	°C.	1/2	1	2	4	20		
1:4	2.10	0	a		+++				
1:6	1.75	0	+		+++				
1:4	1.50	0	0	+	+++				
1:4	1.23	0	0	0	0	0	+++		
1:4	1.03	0	0	0	0	+	+++		
1:4	0.99	0	0	0	+	+++			
1:4	0.95	0	0	0	0	0	0	+in 2 hrs.	
1:4	1.23	R.T.	0	+	+++				
1:4	0.99	R.T.	+	+++					

\* Precipitation set in before all the material dissolved.

A preparation of this type and containing 1.75% of sulfur if added to 4 parts of methyl alcohol at room temperature will not be completely dissolved before a precipitate starts to form and within 30 minutes a heavy precipitate will have formed. From the above table (II) it is evident that arsphenamine II, whose sulfur content equals that of arsphenamine I but whose sulfur has been introduced nearly wholly as sulfonic acid, precipitates very rapidly from conc. methyl alcohol solutions. This type of preparation even when containing a much lower sulfur content than the average toxic arsphenamine I, deposits a precipitate much more rapidly. Again, the precipitation is more rapid at room temperature than at 0°. However, it appears that in this series warming a solution which has given no precipitate in 20 hours at 0° does not cause the sudden formation of a heavy precipitate as was the case in Table I.

The addition of methyl alcoholic-hydrochloric acid to alcoholic arsphenamine solutions also increases the speed of precipitation of the sulfonic acid derivative (Table III).

Experiments were made to determine the extent to which the sulfur content of arsphenamine could be lowered by removal of the sulfonic acid by warming and by the addition of hydrochloric acid at 0° (Table IV). Apparently arsphenamine I upon standing for a long time at room temperature, a short time at 45°, or 20 hours with a small amount of acid

TABLE III  
EFFECT OF ADDITION OF METHYL ALCOHOLIC HYDROCHLORIC ACID TO ARSPHENAMINE SOLUTIONS

Ratio of Arsph. to CH <sub>3</sub> OH to HCl	S Content	Temp.	Time in hours						
			1/2	1	2	4	20	27	
G. : Cc. : G.	%	°C.							
(Arsphenamine I)									
1 : 4 : 0	1.78	0	0	0	0	0	0		
1 : 4 : tr	1.56	0	0	0	0	0	+		++
1 : 4 : 0.05	1.78	0	0	0	0	0	+++		
1 : 4 : 0.05	1.87	0	0	0	0	—	+++		
1 : 3 : 0.04	1.64	R.T.	0	0	+++				
(Arsphenamine II)									
1 : 4 : 0.1	1.23	0	+	+++					
1 : 4 : tr.	1.03	0	0	0	0	++	+++		

<sup>a</sup> After 10 hrs.

TABLE IV  
REMOVAL OF SULFONIC ACID

Ratio of Arsph. to CH <sub>3</sub> OH to HCl	Expt.	Temp. °C	Time Hours	Sulfur content	
				Original %	CH <sub>3</sub> OH-soluble %
G. : Cc. : G					
(Arsphenamine I)					
1 : 4 : 0	2	R.T.	45	1.70	1.27
1 : 4 : 0	3	0 and 45	20 5	1.71	1.29
1 : 4 : 0.05	1	0	20	1.87	1.22
(Arsphenamine II)					
1 : 4 : 0	4	0	20	1.48	0.91

lowers the sulfur content of the material remaining in the alcohol to the same value, 1.26%. However, the decrease never goes as far as in the case of arspenamine II.

It was previously stated that the low sulfur-containing, slightly toxic arspenamines prepared under the most favorable conditions from the nitro acid<sup>6</sup> gave no precipitate from alcoholic solution. Action of heat and hydrochloric acid has been investigated on these solutions. A 1:4 solution of such a sample (0.58% of sulfur) after 20 hours at 0° and 5 hours at 45° showed no trace of yellow precipitate; a similar solution containing 0.05 g. of hydrochloric acid after 23 hours at 0° contained not the slightest precipitate. In addition to proving that arspenamine prepared in this way cannot be forced to deposit sulfonic acid from alcoholic solutions, these experiments prove that these accelerating processes cause only the deposition of that portion of the arspenamine containing the sulfur from alcoholic solutions of high sulfur arspenamine.

When centrifuging the alcoholic solutions in order to remove the precipitated sulfonic acid derivative, it has been found quite difficult to clarify

<sup>6</sup> See THIS JOURNAL, 43, 2202 (1921) for method of preparation.

the liquor when arsphenamine I is being examined, whereas solutions of arsphenamine II deposit the sulfonic acid in such a way that the liquor becomes clear very readily. When hydrochloric acid was used to accelerate the precipitation from Type I the clarification became much easier.

From biological experiments it appears that arsphenamine II causes very slow death while type I frequently kills with great rapidity and always in smaller doses.

All the phenomena reported here and the biological experiments reported in a previous paper show that arsphenamine I differs considerably from arsphenamine II, *i. e.*, arsphenamine which would have low toxicity and low sulfur if the sulfonic acid had not been mixed with the pure amino acid. The great effect produced on the rate of separation of the 5-sulfonic acid derivative from alcoholic solutions of arsphenamine I by the application of heat or small amounts of hydrochloric acid, and the rapid formation of heavy precipitates when solutions which have changed little at 0° are heated, and the fact that solutions of arsphenamine II which do not give a heavy precipitate at 0° will not do so at 45°, might indicate that this substance is not present as such but is produced by rearrangement of some unstable substance.

However, the 5-sulfonic acid derivative of arsphenamine may be present as such in type I and the slow separation which can be greatly accelerated by heat or acid may be due to the colloidal nature of the material. Inasmuch as alcoholic solutions of arsphenamine II, which must contain the sulfonic acid as such on account of the method of preparation, also deposit the sulfur compound more rapidly when warmed or when acidified, the second suggestion seems the more plausible. Very little is known concerning the colloidal nature or state of molecular aggregation of arsphenamine and considerable work must be done along these lines before the problem can be fully understood.

When alcoholic solutions of arsphenamine I are kept at 45° for 20 to 24 hours and are then poured, without separation of the precipitate, into ether, the material is completely recovered with little alteration in sulfur content but with a lower toxicity (Table V).

TABLE V  
RECOVERY WITH ETHER

Ratio of Arsph. to CH <sub>3</sub> OH G.:Cc.	Temp. °C.	Time Hours	Tol. dose		Sulfur content	
			Original	Final	Original	Final
				Mg./kg.	%	
1:5	45	24	50	ca. 80	2.04	
1:5	45	20	ca. 60	90	1.40	1.34

The substance recovered cannot be redissolved in methyl alcohol and acts like a mechanical mixture of arsphenamine and its 5-sulfonic acid. The toxicity has also become the same as that found for arsphenamine II<sup>3</sup>

the alcoholic solution of which deposits a precipitate rapidly at 0°. Heating, therefore, whether by causing a rearrangement or an alteration in colloidal properties, destroys some of the differences between types I and II.

To explain the existing phenomena it will be necessary to obtain a more definite understanding of the mechanism of the reaction and side reactions which take place when the nitro group is reduced and the processes which may occur when the by-products undergo the subsequent reactions. This work is well under way at the present time.

### Summary

Certain chemical and biological differences between high sulfur, highly toxic arsphenamine obtained from the nitro acid and arsphenamine prepared by the reduction of mixtures of the amino acid and its 5-sulfonic acid have been pointed out. Two suggestions have been made regarding the cause of these differences and work has been started to study the mechanism by which the sulfur compounds are formed as a result of hydrosulfite reduction of the nitric acid.

I wish to thank Dr. Reid Hunt for determining the toxicity of the specimens employed in this work.

BOSTON, MASSACHUSETTS

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[CONTRIBUTION FROM THE LABORATORY OF PLANT CHEMISTRY OF THE DEPARTMENT OF BOTANY, UNIVERSITY OF MICHIGAN]

## THE CATALYTIC HYDROGENATION OF DEXTRO GLUCOSE. PRELIMINARY NOTICE

By W. E. CAKE

Received January 19, 1922

In view of all the recent work in the field of catalytic hydrogenation, it is remarkable that there are no accounts in the literature of the catalytic reduction of the sugars to the sugar-alcohols. It would be surmised that in such a reactive molecule as a straight chain hydroxy-aldehyde or hydroxy-ketone, the aldehyde or ketone group would readily lend itself to reduction by hydrogen in the presence of a catalyst.

The behavior of the sugars in neutral and acid solutions is such as to lead to the conclusion that they are not, for the most part, in a straight chain form, but that they exist in a  $\gamma$ -oxide ring form, in which the molecule does not contain an active aldehyde or ketone group. It is usually considered that the two forms are in equilibrium, and that the equilibrium point is far over to the  $\gamma$ -oxide ring side.

In alkaline solution, on the other hand, it seems as though there is quite an appreciable amount of the straight-chain forms present, either, in the case of the aldoses, as the aldehyde hydrate or, what is more likely, as the aldehyde itself in equilibrium with the aldehyde hydrate, together

with a number of enolic forms. This supposition is especially confirmed by the fact that in alkaline solution the simple sugars are known to change over into some of the isomeric forms. *d*-Glucose, for example, is partially converted in alkaline solution into *d*-mannose and *d*-fructose, and it is possible to conceive of the formation of many other sugars as well, in the same solution. The change is supposed to take place through the breaking of the ring with the intermediate formation of the aldehydrol and the enolic forms. In the formation of the first enol from the aldehydrol by loss of water, the  $\alpha$ -carbon atom loses its asymmetry and, conversely, when this enol adds water again, the  $\alpha$ -carbon atom becomes asymmetric, with the consequent formation of two stereo-isomeric aldehydrols, one a derivative of *d*-mannose and the other a derivative of *d*-glucose. These aldehydrols on loss of water are converted into the respective sugars.

The interconvertibility of the sugars in alkaline solution shows that in such solutions there exists an appreciable amount of straight-chain forms, and one would therefore expect the greatest success in catalytic reduction to be not in neutral or acid solutions, but in alkaline.

Should this supposition prove correct, *d*-glucose should yield on reduction the corresponding sugar alcohol *d*-sorbitol. Furthermore, other stereo-isomeric alcohols might be produced because of the transformation of glucose into its isomers. If in alkaline solution *d*-mannose and *d*-fructose are formed from the *d*-glucose aldehydrol, we should expect to find *d*-mannitol also as a reduction product, in addition to *d*-sorbitol. The determining factor for the proportion of *d*-mannitol in the alcohols resulting from the reduction of *d*-glucose would probably be the rate of hydrogenation. If the reduction were carried on fast enough to use up all the aldehyde as fast as formed from the ring form, then we should expect to find only *d*-sorbitol as a reduction product of *d*-glucose, even in alkaline solution. Of course, if it were possible to carry out this reduction in neutral or acid solution, *d*-sorbitol would then be the only product regardless of the rate of hydrogenation.

There is a further possibility of the mechanism of the reduction of the simple sugars in alkaline solution that must be considered. The various enolic forms present in such solutions all contain a double bond between two carbon atoms, to each of which a hydroxyl group is attached. It is possible to conceive that the reduction occurs at this point by the addition of two atoms of hydrogen. In this event we should always expect to find more than one alcohol as the reduction product of any sugar, since either one or two carbon atoms are rendered asymmetric, depending upon the particular enol in question.

### Experimental Part

In order to test these points, 200 cc. of a 25% solution of *d*-glucose in 0.5 *N* potassium hydroxide solution was treated with hydrogen in the presence of about 3 g. of platinum

black. The hydrogen was introduced rapidly enough to keep the liquid in considerable agitation and the platinum thoroughly stirred. After 18 hours the solution had lost all of its reducing action on Fehling's solution. When the platinum had settled, the clear colorless liquid was siphoned off, and from it *d*-sorbitol and *d*-mannitol were obtained, using the procedure outlined by Fischer<sup>1</sup> in separating the products of reduction of *d*-fructose by sodium amalgam. The solution was first neutralized with dil. sulfuric acid and then concentrated on a water-bath until most of the potassium sulfate separated from the solution. To this was added 8 times the volume of boiling absolute alcohol, and the precipitated potassium sulfate removed by filtration. After concentrating a little the solution was cooled, whereupon the mannitol separated in the form of fine needle-like crystals, which after purification by recrystallization from 70% alcohol melted at 166°.

The combined filtrates from the recrystallization of the mannitol, and from the original mannitol precipitation, were concentrated on a water-bath, with the addition of water from time to time, until the alcohol was removed, and finally evaporated to a volume of about 50 cc. From this solution the sorbitol was recovered according to the directions of Meunier.<sup>2</sup> After cooling to 0°, an equal volume of 60% sulfuric acid was added, and then the acid solution was shaken with 35 cc. of benzaldehyde. On standing overnight at 0°, there separated a large quantity of the white amorphous dibenzal derivative of sorbitol. This was filtered, washed with a little water and ether, and then hydrolyzed with boiling 5% sulfuric acid. After cooling the liberated benzaldehyde was shaken out with ether, and the sulfuric acid just neutralized with a solution of barium hydroxide. The resulting solution was filtered and concentrated to a thick sirup, to which was added on cooling a little 95% alcohol. The sirup soon solidified and was dried by pressing between filter paper. This was now dissolved in a little hot 90% alcohol and, on standing, the solution soon deposited the sorbitol in the form of colorless clusters. These were filtered, washed with a little alcohol and finally dried in a vacuum desiccator over conc. sulfuric acid. The sorbitol so obtained melted at 73–75°.

Work is now being conducted in this laboratory on the catalytic hydrogenation of the several sugars, under the influence of various catalysts and various conditions of acidity and alkalinity, temperature and pressure. It is expected to show what alcohols result from the sugars under these varying conditions and in what proportions they are formed.

Up to the present, all attempts to reduce *d*-glucose in neutral solution have proved futile. However, if the hydrogenation is conducted under pressure or in the presence of more active catalysts, it may prove possible to do this.

The platinum black used as the catalyst was prepared by a slight modification of the method of Willstätter and Waldschmidt-Leitz,<sup>3</sup> in which dry potassium chloroplatinate suspended in a 20% formaldehyde was reduced, instead of starting with an acid solution of chloroplatinic acid.

### Summary

Preliminary notice of the catalytic hydrogenation of the sugars is given.

ANN ARBOR, MICHIGAN

<sup>1</sup> Fischer, *Ber.*, 23, 3684 (1890).

<sup>2</sup> Meunier, *Compt. rend.*, 110, 579 (1890). *Ann. chim. phys.*, [6] 22, 412 (1891).

<sup>3</sup> Willstätter and Waldschmidt-Leitz, *Ber.*, 54, 113 (1921).

[CONTRIBUTION FROM THE HAVEMEYER CHEMICAL LABORATORY OF NEW YORK UNIVERSITY AND THE CHEMICAL LABORATORY OF IOWA STATE COLLEGE]

## DYES CONTAINING THE FURANE CYCLE<sup>1</sup>

BY R. R. RENSHAW AND NELLIE M. NAYLOR<sup>2</sup>

Received January 21, 1922

In the present paper the preparation and properties of certain dyes derived from furfural are described. Preliminary experiments on this line were carried out in the spring of 1915, and it is felt certain that the present authors were the first to isolate stable dyes containing the furane cycle.

On account of the activity of others in this field since the first public announcement of our work was made,<sup>3</sup> it seems desirable to present these results at this time. Our intention was to enlarge considerably the scope of the work,<sup>3</sup> but on account of the entry of one of us into war activities and a subsequent change of location this has been impossible.

Highly colored, unstable condensation products of furfural with primary and secondary aromatic amines have been studied in considerable detail by a number of investigators, notably Stenhouse,<sup>4</sup> H. Schiff,<sup>5</sup> de Chalmot,<sup>6</sup> Ehrhardt,<sup>7</sup> Knovenagle,<sup>8</sup> Zincke and Muhlhausen,<sup>9</sup> Dieckmann and Beck<sup>10</sup> and Konig.<sup>11</sup> None of these products, however, was of any value as a dye.

The condensation of furfural with dimethyl aniline was carried out by O. Fischer<sup>12</sup> at the time that he discovered malachite green by oxidizing the condensation product of benzaldehyde with that base. He found that the leuco base of malachite green, tetramethyl-diamino-triphenyl-methane, was colorless, while the leuco base of the corresponding compound obtained by using furfural instead of benzaldehyde, tetramethyl-diamino-diphenyl-furyl-methane, was light yellow, yet on the oxidation of these two leuco compounds he obtained on the one hand malachite

<sup>1</sup> Read at the Buffalo Meeting of the American Chemical Society, April 6, 1919.

<sup>2</sup> The results described in this paper furnished part of the material submitted in a thesis for the degree of Master of Science at Iowa State College in June, 1918, by Nellie M. Naylor.

<sup>3</sup> In 1913 the senior author began an investigation of corn cobs as a possible source of pentose sugars (U. S. patent 1,190,953) and other materials derived from pentosans, as fermentation products and furfural.

<sup>4</sup> Stenhouse, *Ann.*, 156, 199 (1870).

<sup>5</sup> H. Schiff, *ibid.*, 201, 355 (1880); 239, 349 (1887).

<sup>6</sup> de Chalmot, *ibid.*, 271, 11 (1892).

<sup>7</sup> Ehrhardt, *Ber.*, 30, 2012 (1897).

<sup>8</sup> Knovenagle, *ibid.*, 31, 2613 (1898).

<sup>9</sup> Zincke and Muhlhausen, *ibid.*, 38, 3824 (1905).

<sup>10</sup> Dieckmann and Beck, *ibid.*, 38, 4122 (1905).

<sup>11</sup> Konig, *J. prakt. Chem.*, [2] 72, 555 (1905); 88, 193 (1913).

<sup>12</sup> O. Fisher, *Ber.*, 10, 1626 (1877); *Ann.*, 206, 141 (1883).

green, a bluish-green dye, and on the other a solution of a product which gave a more *yellow-green* color than the former and which was very unstable to light. He supposed this to be the furane analog of malachite green.

On reviewing this work of Fisher the present authors were struck by the apparent inconsistency that the furyl group when substituted for the phenyl group in the leuco base and in the dye had an opposite effect on the absorption of light by the compounds. The furyl group in the leuco compound brought about a greater absorption in the visible spectrum than the phenyl group (yellow and colorless), while in the oxidation product the furyl group seemed to absorb less, that is, the furyl derivative gave a yellow-green color while the phenyl derivative gave a blue-green color.

It was decided to repeat Fisher's work in order to determine with certainty the color of tetramethyl-diamino-diphenyl-furyl-methane. If this were in fact yellow then theory would demand that the dye obtained from it by oxidation (if of analogous structure to malachite green) should absorb more light than the latter. Of course there was the possibility that in the oxidation, the furane nucleus was opened and a compound similar to Konig's azomethin dyes was obtained. However, there is no evidence that such a compound could be formed from tertiary amines.

Experiments proved that tetramethyl-diamino-diphenyl-furyl-methane does absorb light in the visible spectrum and has a light yellow color. Our theoretical considerations were fully borne out as to the color of the salts of its oxidation product. The furane analog of malachite green was obtained both as the zinc chloride double salt and as the oxalate by the oxidation of the leuco compound. These salts and their solutions are more deeply colored than is malachite green, and much to our surprise the colors of fabrics dyed with this substance are indistinguishable as to degree of stability from the former as shown by the standard tests of fastness to light, perspiration, acid, alkali, hydrogen peroxide, milling, stoving, etc.

The dye gives gray-blue shades on silk, wool, and mordanted cotton. Like malachite green the shade on cotton is not a pure tone, but on wool and particularly on silk very handsome effects are obtained.

Attempts were made to prepare other types of dyes containing the furane nucleus. An example of an hydroxy-ketone dye was prepared by the condensation of pyromucic acid with pyrogallol. It is presumably the furane analog of alizarin yellow A, trihydroxyphenyl-furyl-ketone. This has a brown color, and forms brown, gray-brown and yellow-brown lakes with aluminum, chromium and iron, respectively. It gives a dark tan color on cotton mordanted with turkey red.

A number of attempts were made to bring about the condensation of



pyromucic acid with gallic acid to form the furane analog of anthracene brown (anthragallo) without success. The presence of gallic acid seemed, unexpectedly, to augment the carbonization of the pyromucic acid by the condensation agents used, zinc chloride and sulfuric acid.

### Experimental

**Preparation of Tetramethyl-diamino-diphenyl-furyl-methane.**—This product was prepared by the standard procedure using zinc chloride as the condensing agent. The leuco base obtained was subjected to exhaustive purification by solution in acid and precipitation with a base, treating with bone black its solutions in aqueous acids and in neutral organic solvents, and final recrystallizations from petroleum ether. The crystals obtained were light yellow, and the color tone was pure, giving a further indication that the color was an intrinsic property of the substance.

**Preparation of the Furane Analog of Malachite Green.**—The leuco base was oxidized with lead peroxide in acid solution in the usual manner. It was desirable to keep the reaction mixture cold, and stir continuously for 2 hours or more. After the elimination of the excess of lead salts, a concentrated solution of zinc chloride was added and the zinc chloride double salt of the dye salted out with sodium chloride. It separated as very dark blue crystals having a bronze reflex. The *oxalate* was prepared from a portion of the dye solution. The dye base was precipitated with sodium hydroxide and thoroughly washed and filtered. It was then treated with a warm saturated solution of oxalic acid, and the mixture filtered warm. The oxalate separated as copper colored needle crystals. They were somewhat soluble in cold water, in ethyl and amyl alcohol and in acetone.

The dye was analyzed by dissolving a well-washed sample of the dye base in hydrochloric acid, filtering and precipitating the chloroplatinate with platinic chloride. The precipitate was washed with alcohol, dried and ignited.

**Analyses.** Calc. for  $C_{21}H_{24}ON_2Cl_4Pt.H_2O$ : Pt, 26.16. Found: 25.95, 25.96.

**The Condensation of Pyromucic Acid with Pyrogallol.**—Six g. each of pyromucic acid and pyrogallol were heated with 18 g. of anhydrous zinc chloride. The reaction began at  $110^\circ$  and was almost complete at about  $125^\circ$ . The product was heated to  $145^\circ$  until no more gas was evolved, and then ground with hot water to dissolve the excess of the reagents. It was purified by solution in sodium hydroxide and precipitation with hydrochloric acid. So obtained it is a yellow-brown powder, melting at  $160^\circ$  (uncorr.). It is soluble in alcohol and in acetone, and insoluble in petroleum ether and benzene. These solvents may be used for its purification.

The product was dyed on cotton by the method used for alizarin. A dark tan shade was obtained.

### Summary

1. It is believed that the present authors were the first to show that stable dyes could be obtained from furfural aldehyde and from pyromucic acid.

2. Contrary to the results obtained by O. Fisher but in accordance with theory the furane analog of malachite green has a deeper color than the latter. It is an equally stable dye and gives a handsome effect on silk and wool.

NEW YORK, N. Y.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

## THE CLARIFICATION OF SOLUTIONS CONTAINING REDUCING SUGARS BY BASIC LEAD ACETATE. THE EFFECT OF DIFFERENT DELEADING AGENTS

BY DUANE T. ENGLIS AND CHUK YEE TSANG

Received January 23, 1922

The use of basic lead acetate as a clearing agent for solutions in which reducing sugars are to be determined is contrary to general practice in sugar analysis.

The work of Bryan,<sup>1</sup> Prinsen Geerligs<sup>2</sup> and others has clearly shown that loss of some reducing sugars, particularly fructose, accompanies its use. Several explanations have been advanced to account for this loss. W. A. Davis<sup>3</sup> contends that in dilute solutions there is no precipitation of fructose by the basic lead acetate even in the presence of chlorides, sulfates or carbonates if only a slight excess of the reagent is used and this excess removed immediately. The change in polarization he concludes is due to a conversion of fructose to glucose. Although this transformation probably does take place on long standing of the fructose in contact with the basic lead solution, nevertheless the work of Doerr<sup>4</sup> and of Pellet<sup>5</sup> demonstrates that the loss is due chiefly to the entrainment of the reducing sugars by the insoluble lead salts, since on decomposing the lead precipitate with sulfuric acid, practically the entire quantity of sugar lost is recovered. Such an entrainment may take place not only in the original clarification process but also in the subsequent deleading procedure when an excess of the reagent has been employed.

Pellet<sup>6</sup> has pointed out that the quantity and nature of the impurities, the amount of lead acetate used, and the concentration of the sugar solution, affect the quantity of sugar carried down. The nature of the impurity has usually received only passing notice. Still, its importance has been indicated.

In a study of the carbohydrates of the Snowdrop (*galanthus nivalis*) Parkin<sup>7</sup> investigated the effect of addition of tannin to a dilute sugar solution containing a mixture of sucrose, glucose and fructose and its removal by basic lead acetate. A very close agreement in rotation and copper reducing power was observed for the treated solution and a blank. In the analysis of molasses Meade and Harris<sup>8</sup> have found that even with the use of neutral lead acetate for clarification purposes, quite varied results are obtained when different deleading agents are used.

In view of these facts it appears that the nature of the lead precipitant is a very important consideration. It seems desirable then to determine the specific effect of different deleading agents in order that it may be ascertained whether the reported loss of sugars is due chiefly

<sup>1</sup> Bryan, *Bur. Chem. Bull.*, 116, 73 (1908).

<sup>2</sup> Geerligs, *Z. ver. deut. Zucker-Ind.*, 59, 761 (1908). *Intern. Sugar J.*, 11, 276 (1909).

<sup>3</sup> Davis, *J. Agr. Sci.*, 8, 1 (1916).

<sup>4</sup> Doerr, *Intern. Sugar J.*, 18, 402 (1916).

<sup>5</sup> Pellet, *Ann. chim. anal.*, 21, 217 (1916).

<sup>6</sup> Pellet, *Bull. assoc. chim. suc. dist.*, 35, 186 (1917).

<sup>7</sup> Parkin, *Biochem. J.*, 6, 12 (1911).

<sup>8</sup> Meade and Harris, *J. Ind. Eng. Chem.*, 8, 504 (1916).

to entrainment by precipitation of impurities naturally present in a plant extract or, perhaps, in some cases at least due in a large measure to the insoluble salts formed by the deleading agent.

### Experimental Part

About 5 g. of glucose was dissolved in water and made up to 500 cc. A solution of lead acetate was prepared according to the official method<sup>9</sup> From the dextrose solution 50cc. portions were measured into each of six 100cc. volumetric flasks. One was set aside as a blank and to each of the others 10 cc. of basic lead acetate was added. Solutions of the various salts indicated below, which were selected as representative deleading agents, were then added to the various flasks in a quantity which had been previously determined as just sufficient to precipitate 10 cc. of the basic lead acetate solution. All were made up to 100 cc., mixed thoroughly and filtered. Reducing sugar in 25cc. portions of the filtrates was determined by the method of Brown-Morris-Millar.<sup>10</sup>

The experiment was then repeated, using instead of glucose a fructose solution of about the same concentration.

The results are indicated in Table I below.

TABLE I  
EFFECT OF DELEADING AGENTS ON ENTRAINMENT OF GLUCOSE AND FRUCTOSE  
Precipitates not washed

Deleading agent	Glucose	Per cent. after deleading <sup>1</sup>	Fructose	Per cent. after deleading	Deleading agent	Glucose	Per cent. after deleading	Fructose	Per cent. after deleading
	G. of CuO		G. of CuO			G. of CuO		G. of CuO	
Blank	0.3045		0.2737		K <sub>2</sub> SO <sub>4</sub>	0.2680	87	0.1675	60
	0.3040		0.2765			0.2630		0.1670	
K <sub>2</sub> C <sub>2</sub> O <sub>4</sub>	0.2895	96	0.1790	65	KNaC <sub>4</sub> H <sub>4</sub> O <sub>6</sub>	0.2700	90	0.2295	81
	0.2910		0.1800			0.2720		0.2300	
Na <sub>2</sub> HPO <sub>4</sub>	0.2930	92	0.2725	98	Na <sub>2</sub> CO <sub>3</sub>	0.2810	93	0.2528	91
	0.2940		0.2730			0.2785		0.2549	

Since the presence of the precipitate would tend to counterbalance some loss of sugar carried down by the lead precipitate another experiment was performed with this variation: the solutions were filtered and precipitates washed until the volume of the filtrate was 200 cc. In addition to the salts tannic acid was introduced as a lead precipitant. The results are recorded in Table II.

<sup>9</sup> "Methods of Analysis A. O. A. C." p. 74, 1920.

<sup>10</sup> Brown, Morris and Millar, *J. Chem. Soc.*, 71, 281 (1897).

TABLE II  
EFFECT OF DELEADING AGENTS ON ENTRAINMENT OF GLUCOSE AND FRUCTOSE  
Precipitates washed

Deleading agent	Glucose	Per cent. after deleading	Fructose	Per cent. after deleading	Deleading agent	Glucose	Per cent. after deleading	Fructose	Per cent. after deleading
	G. of CuO		G. of CuO			G. of CuO		G. of CuO	
I Blank	0.1565		0.1425		V $\text{KNaC}_4\text{H}_4\text{O}_6$	0.1486	93	0.1320	95
	0.1580		0.1430			0.1480		0.1350	
II $\text{K}_2\text{C}_2\text{O}_4$	0.1530	98	0.1185	85	VI $\text{Na}_2\text{CO}_3$	0.1514	95	0.1250	90
	0.1540		0.1160			0.1510		0.1255	
III $\text{Na}_2\text{HPO}_4$	0.1570	99	0.1402	99.5	VII Tannic acid	0.1570	99	0.1410	99.6
	0.1565		0.1400			0.1560		0.1400	
IV $\text{K}_2\text{SO}_4$	0.1410	91	0.1132	82					
	0.1405		0.1100						

### Discussion and Conclusions

It is shown from these experiments that the loss of reducing sugars varies greatly when different insoluble lead salts are thrown out of solution by basic lead acetate. The loss of fructose is in general much greater than that of glucose, which result is in accord with those of previous workers. It is quite interesting that carbonates, sulfates and oxalates, which have been perhaps most extensively employed as deleading agents cause most marked losses while with disodium phosphate the loss is nearly negligible. The use of disodium phosphate seems to have an added advantage, in that a clear filtrate is nearly always obtained, while with some of the other deleading agents there is a great tendency to give turbid filtrates. With tannic acid a very slight loss is to be noted. If tannin may be taken as a representative of natural impurities in plant extracts it would seem that loss of sugar, due to the deleading agents, may be as great as that of the natural impurity in case a large excess of basic lead acetate was used in the original clarification procedure.

The loss of sugar appears to be caused primarily by occlusion in the lead precipitate, since on washing the precipitate a much smaller loss is observed.

### Summary

A comparative study has been made of the effect of removal of basic lead acetate from solutions of glucose and fructose by means of potassium oxalate, disodium phosphate, potassium sulfate, potassium sodium tartrate and sodium carbonate. With glucose the quantity of sugar carried down by the lead precipitates, as indicated by loss in reducing power, varies from less than 1% to as much as 10%; with fructose, from less than 1% to as much as 35%. Disodium phosphate seems to be the most satisfactory deleading agent.

URBANA, ILLINOIS

[CONTRIBUTION FROM THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY, LABORATORY OF ORGANIC CHEMISTRY]

## THE ACTION OF SULFURIC ACID ON NITROGUANIDINE<sup>1</sup>

By TENNEY L. DAVIS

Received January 27, 1922

Nitroguanidine is an especially interesting and valuable explosive for the reasons that it is cool, and that it may be produced cheaply from raw materials the supply of which is inexhaustible. While it has about the same force as 75% dynamite, Vielle's experiments<sup>2</sup> have shown that its explosion produces a temperature of only 907° as compared with 3161° for 75% dynamite, 3429° for mannite hexanitrate, and 2676° for the nitro-cellulose powder of the French. Since dicyandiamide reacts<sup>3</sup> with 2 molecules of ammonium nitrate to yield 2 of guanidine nitrate, and since guanidine nitrate on treatment with strong sulfuric acid gives nitroguanidine<sup>4</sup> in excellent yield, the explosive can be prepared by a short process from atmospheric nitrogen—and the action of sulfuric acid on nitroguanidine is a matter of obvious and immediate interest.

If nitroguanidine is dissolved in cold conc. sulfuric acid and the solution is diluted promptly with water, the material precipitates again. If the solution is allowed to stand, gas bubbles presently begin to come off and the solution after a few days no longer gives any precipitate when diluted with water. The same gas evolution and destruction of nitroguanidine take place more quickly if the solution in strong sulfuric acid is warmed. In view of these facts it is necessary to operate rapidly and at as low a temperature as possible when preparing nitroguanidine from guanidine nitrate by the action of sulfuric acid.

Preliminary experiments showed that the gases contain nitrous oxide and carbon dioxide and that ammonium sulfate remains in the acid liquid—a result which leads us to believe that the decomposition of nitroguanidine by strong acid might be the same as the reported decomposition by strong alkali,<sup>5</sup> namely, in accordance with the following equation.



We have shown this to be the case by measurements of the amounts of ammonia and of carbon dioxide. These are produced quantitatively

<sup>1</sup> This investigation was carried out in connection with a contract between the Ordnance Department and the Massachusetts Institute of Technology, and the present paper is published by permission of the Chief of Ordnance. In this work I have been assisted by A. A. Morton. T. L. D.

<sup>2</sup> Vielle, "Mémorial des Poudres," 11, 195 (1901).

<sup>3</sup> THIS JOURNAL, 43, 2234 (1921). Compare also Ewan and Young, *J. Soc. Chem. Ind.*, 40, 109-12T (1921).

<sup>4</sup> Jouselin, *Compt. rend.*, 88, 1087 (1879). Pellizzari, *Gazz. chim. ital.*, 21, II, 406 (1891).

<sup>5</sup> Franchimont, *Rec. trav. chim.*, 10, 233 (1891). Thiele, *Ann.*, 270, 18 (1892).

in accordance with the equation when a solution of nitroguanidine in sulfuric acid is evaporated until fumes come off. The reaction has a possible application as a means of analysis.

Nitroguanidine dissolved in dil. sulfuric acid can obviously not be recovered by the evaporation of the solution. We have determined the solubility of nitroguanidine in sulfuric acid of various concentrations by measurements of the amount of carbon dioxide which is produced when the solutions are evaporated to fuming. We have been able to check these results by digesting known weights of nitroguanidine with dil. sulfuric acid in the thermostat and measuring the loss in weight.

### Discussion of Experiments

The nitroguanidine which was used for this work was a sample which had been recrystallized from water to constancy of melting point. When the temperature of the melting-point bath was raised with moderate rapidity, the sample melted sharply at  $232^{\circ}$  and decomposed at a slightly higher temperature giving off gas and depositing a white solid.

A weighed amount was heated with sulfuric acid, the acid liquid was made slightly alkaline with caustic soda and distilled with steam as in the Kjeldahl determination of ammonia, and the distillate was titrated with standard hydrochloric acid solution. The ammonia which was found, therefore, was the result both of the acid and of the alkaline decomposition, but the fact that ammonia was produced quantitatively only when the sulfuric acid solution had been evaporated to fuming is evidence that the

Wt. of sample G.	Acid Cc.	Materials	Duration of heating Hours	Conditions of heating	NH <sub>3</sub> %
0.2638	{ 10 50	{ conc. acid water }	1	Reflux condenser	83.33
0.4271	Same		3	Reflux condenser	68.0
0.6788	{ 15 100	{ conc. acid water }	4	Same	64.1
0.8717	{ 10 1	{ conc. acid water }	2	Fuming in Kjeldahl flask	100.6
0.9664	Same		2	Boiled under reflux	97.0
0.7751	{ 8 5	{ conc. acid water }	2	Same	69.3
1.1484	{ 2 10	{ fuming acid conc. acid }	2	Fuming in flask	99.93
1.5328	{ 2 132	{ fuming acid conc. acid }	2	Not fuming	61.87
2.0712	{ 10	{ conc. acid }	3	Not fuming	71.31
1.2044	{ 3 8	{ fuming acid conc. acid }	3	Fuming	99.4
1.5941	10	conc. acid	3	Fuming in covered casserole	99.6
1.1484	Same		3	Same	99.93

alkaline decomposition in our experiments was inconsiderable and that the vigor of the sulfuric acid treatment was the determining factor. It was found necessary, when working with conc. sulfuric acid, to start the heating slowly; otherwise small explosions occurred involving possible loss of material. The various experiments are tabulated below, where the conditions under which each experiment was carried out are indicated. The *per cent.* is the amount of ammonia which was found calculated as a fraction of the amount which would be expected in accordance with the above equation. Results were satisfactory in the cases in which the liquid was evaporated to fuming.

Vigorous heating was found to be necessary also for the liberation of all of the carbon dioxide from nitroguanidine. Satisfactory results were obtained by dissolving the sample in dil. sulfuric acid and evaporating until crystals of ammonium sulfate separated from the liquid. Rather elaborate apparatus was necessary in order that no part of it might be attacked by sulfuric acid fumes and in order that sulfuric acid and water might be completely removed from the gases before they reached the tubes for the absorption of carbon dioxide. As the solution became concentrated, it was necessary to continue the heating more slowly in order to avoid a violent evolution of gas.

Wt. of sample G.	Acid Cc.	Materials	Duration of heating Hours	Conditions of heating	CO <sub>2</sub> %
0.3028	{ 10 5	{ conc. acid water }	1/2	Boiled slowly	93.9
0.2815	Same		1/4	Same	55.0
0.7906	{ 20 10	{ conc. acid water }	1/2	Same	54.0
0.8500	{ 30 5	{ conc. acid water }	3	Same	97.77
*2.6994	{ 4 2.5	{ conc. acid water }	1 1/2	Boiled until crystals appeared	99.47
*1.9735	Same		Same	Same	99.93
1.9593	Same		Same	Same	99.95
1.7374	Same		Same	Same	99.90
1.4489	Same		Same	Same	100.11

In the two experiments which are marked with a star, 0.4 g. of potassium permanganate was added in the expectation that it would hasten the decomposition of the nitroguanidine. It was found however to be without material effect.

Samples of nitroguanidine were digested with sulfuric acid of various concentrations (the specific gravity was determined) in a well-regulated thermostat at 25° for periods of at least 3 days. A measured volume of the saturated solution was then removed, and nitroguanidine was determined in it by weighing the carbon dioxide which it evolved when heated

as described above. Similar experiments were carried out with samples digested, with frequent shaking, in ice water for at least 3 days. Results are shown in the following table.

Sulfuric acid		Nitroguanidine (g.) per 100 cc. of solution	
Sp. gr.	%	at 0° G.	at 25° G.
1.092	13.2	...	0.3418
1.120	17.0	0.2498	0.6162
1.132	18.5	0.4438	0.8988
1.160	22.2	0.5324	1.357
1.187	25.6	0.5822	1.909
1.219	29.7	1.107	2.815
1.269	35.6	...	5.348
1.355	45.4	5.368	10.81

In order to check these results another set of determinations was made by a different method. An excess of nitroguanidine, previously dried to constant weight and weighed, was placed in each of seven 250cc. glass-stoppered narrow-mouth bottles; 150cc. portions of dil. sulfuric acid of known specific gravity were introduced into the bottles, and the bottles were shaken in the thermostat at 25° for 10 hours. The contents of each bottle was filtered immediately through a weighed Gooch crucible, drained as much as possible, carefully washed with 25 cc. of ice water, dried to constant weight at 100° and weighed. The solubility of the nitroguanidine was calculated on the basis of the amount which was left undissolved. Another series was carried out in the same way except that the bottles after removal from the thermostat were kept in ice water for 2 days with frequent shaking. These experiments were made in duplicate. The results tabulated below are the means of two determinations.

Sulfuric acid		Nitroguanidine per 100 cc. of solution	
Sp. gr.	%	at 0° G.	at 25° G.
1.12	17.0	0.447	0.700
1.13	18.3	0.495	0.920
1.15	20.9	0.664	1.280
1.18	24.8	0.755	1.800
1.22	29.8	1.506	2.714
1.26	34.6	...	5.451
1.349	44.7	6.956	11.129

In the accompanying graph the values obtained by determination of carbon dioxide are indicated by crosses while those obtained by difference of weight before and after treating with solvent are indicated by black dots. It appears that the two methods give substantially the same result.

The mean curves are plotted. Reading from them we obtain the following figures for the solubility of nitroguanidine in sulfuric acid of various



concentrations. The values for pure water, determined by the usual method, are included for purposes of comparison.

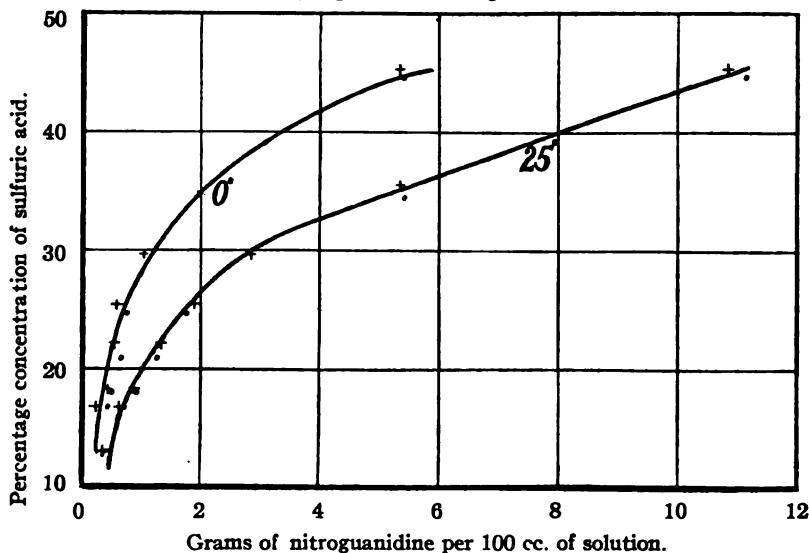


Fig. 1.—Solubility of nitroguanidine in sulfuric acid of various concentrations.

Conc. of sulfuric acid used %	Nitroguanidine per 100 cc. of solution	
	at 0° G.	at 25° G.
45	5.8	10.9
40	3.4	8.0
35	2.0	5.2
30	1.3	2.9
25	0.75	1.8
20	0.45	1.05
15	0.30	0.55
0	0.12	0.42

### Summary

Nitroguanidine is decomposed quantitatively by hot conc. sulfuric acid, half of its nitrogen appearing as ammonia and all of the carbon as carbon dioxide. By taking advantage of this reaction to determine the solubility of nitroguanidine in sulfuric acid of various concentrations, results have been obtained which check with those determined by the more direct method.

CAMBRIDGE 39, MASSACHUSETTS

## NOTE

**Correction.**—On p. 2374 of the article by Adams, Bramlet and Tendick, in *THIS JOURNAL*, 42, 2369 (1920), starting with the heading "Methylanilide of Pyruvic Acid," read as follows.

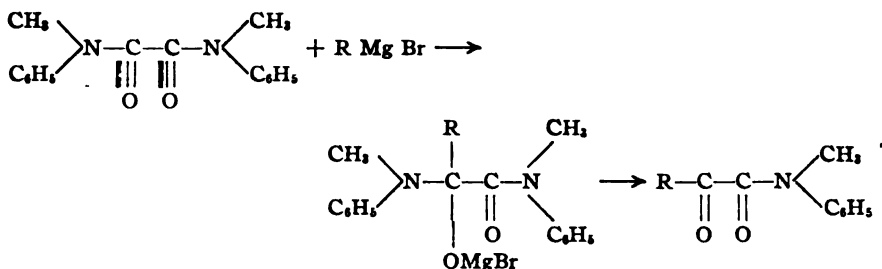
**Methylanilide of Pyruvic Acid.**—To 4 moles of methyl-magnesium iodide, 1 mole of dimethyl-oxanilide was added gradually. The reaction was worked up as described under the preparation of the methylanilide of  $\alpha$ -ketobutyric acid. The product formed a light yellow oil which when pure boils at 148–150° at 10 mm.

*Analysis.* Subs., 0.1626: 10.2 cc.  $N_2$  (27° and 765 mm.). Calc. for  $C_{11}H_{11}O_2N$ : N, 7.9. Found: 8.1.

**Methylanilide of Benzoylformic Acid.**—An excess of phenyl-magnesium bromide was treated with 1 mole of dimethyl-oxanilide and the product worked up in the way described above. From the ether solution, a brown oil was obtained. This oil solidified to a crystalline mass after 48 hours. The crystals are sucked dry from the oil, washed with a little petroleum ether and ether and finally crystallized from the same mixture. White needles melting at 83–84° were obtained.

*Analysis.* Subs., 0.2230: 11.6 cc.  $N_2$  (24° and 765 mm.). Calc. for  $C_{11}H_{11}O_2N$ : N, 5.8. Found: 6.0.

The second and third structural formulas in the reaction given at the top of p. 2371 are incorrectly formulated. They should be as follows.



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ROGER ADAMS

## NEW BOOKS

**Report of the American Committee on Electrolysis.** American Institute of Electrical Engineers, 33 West 39th Street, New York, N. Y., 1921. 204 pp. 33 figs. 15 × 24 cm. Price \$1.00.

The American Committee on Electrolysis has just issued its 1921 report, superseding its preliminary report of 1916. This report embodies such statements of facts and descriptions, and discussions of methods of electrolysis testing and electrolysis mitigation as the members of the committee have been able thus far to agree upon unanimously. In the preface, signed by Bion J. Arnold, Chairman of the Committee, the following statement is made:

"While this report supersedes the preliminary report of 1916, it should, unless the principals see fit to discontinue the work of the main committee, be considered as in the nature of a progress report and not as final, as it is impossible at the present time to finally answer many of the outstanding questions involved. Also it is to be understood that the report is confined to the technical and engineering aspects of the subject and does not attempt to deal with matters of policy or with legal questions, such as the rights and responsibilities of the several interests concerned."

The report comprises five chapters. Chapter I sets forth a rather full statement of principles and definitions. Chapter II is devoted to a somewhat detailed discussion of the design, construction, operation, and maintenance of railways and underground structures affected by electrolysis, and to a discussion of questions involving the interconnection of affected structures and railways, ending with a summary of good practice as agreed upon by the committee. Chapter III gives a discussion of the fundamentals of the whole question of electrolysis surveys, their purpose, scope, possibilities, and interpretation, and also a discussion of the instruments suitable for electrolysis testing. Chapter IV is devoted to an analysis of present European practice relating to electrolysis mitigation. In Chapter V the committee outlined certain researches which it deems necessary to have carried out in order to make it possible to reach a final solution of some of the fundamental questions pertaining to electrolysis mitigation.

The American Committee on Electrolysis which prepared this report is a joint committee having three representatives from each of the following organizations.

American Institute of Electrical Engineers  
American Electric Railway Association  
American Gas Association  
American Railway Engineering Association  
American Telephone and Telegraph Company  
American Water Works Association  
National Electric Light Association  
Natural Gas Association  
National Bureau of Standards

BURTON MCCOLLUM

**A Laboratory Manual of General Chemistry.** By JAMES H. WALTON, Ph. D., Professor of Chemistry, Univ. of Wisconsin, and FRANCIS C. KRAUSKOPF, Ph. D., Associate Professor of Chemistry, Univ. of Wisconsin. The Collegiate Press, George Banta Publishing Co., Menasha, Wis., 1920. v + 172 pp. 7 figures. 16 × 23.5 cm.

This manual includes about one hundred and fifty experiments, and seems especially adapted to the use of a class in which some, but not all, of the students have had a preliminary school course. "A number of time-honored experiments of doubtful value have been left out. In particular, many test-tube experiments which teach isolated facts and furnish information of an encyclopedic nature only have also been omitted." Alternate pages of the manual are blank, and are apparently to be used instead of a notebook for "the (necessarily brief) record of observations, inferences, equations, answers to questions, etc." The book is rather bulky, due to the introduction of these blank pages, and to the inclusion of a detailed outline (39 leaves) of the first semester's work. This is intended to teach the beginning college student how to outline his work, and should serve the purpose admirably. There are also examination questions and problems, appendices on "Units of Measurement," "Charles' Law and Boyle's Law," "Important Elements and Some of Their Physical Properties," and "Activity Series of the Metals," and a classified list of references for outside reading. The usual lists of apparatus, chemicals, and tables of the vapor pressure of water, etc., complete the book.

The experiments are well suited to beginners of college grade, and some of them will also interest freshmen who have had a good high-school course, but a larger proportion of more difficult experiments and preparations on a slightly larger scale would, in the reviewer's opinion, make the book more valuable for the latter class of students. Experiment 98 on osmotic pressure is ingenious, and so is Experiment 20 on velocity of crystallization.

A certain lack of care in expression is noticeable. "To just melt," "to just touch," "to first wash," and similar constructions are of frequent occurrence. There seem to be misprints in the "Caution" on p. 6, and in the heading of Expt. 138.

NORRIS F. HALL

**Zeittafeln zur Geschichte der organischen Chemie** (Chronological Tables of the History of Organic Chemistry). By PROF. DR. EDMUND O. VON LIPPMANN, Dr. Ing. E. H. at the Technische Hochschule, Dresden, Director of the Zuckerraffinerie Halle, Halle a.S. Julius Springer, Berlin, 1921. Paper covers; 67 pages with index 17 × 25 cm. Price 18 Marks in Germany, 54 Marks in America.

The many readers of Prof. Lippmann's essays upon scientific and historical subjects will welcome his new "chronological tables of the history of organic chemistry." This little work developed from the author's growing collection of historical notes, the complete absence of indexes in the recent histories of organic chemistry by Hjelt and by Graebe and

the demand for a convenient source-book of information finally influencing him to attempt its publication.

Prof. Lippmann begins his chronology at the year 1500 with oil of absinthe, first mentioned in Brunschwig's "Distillirbuch" and closes it at the year 1890 with the centric naphthalene formula of Bamberger. Within this compass he mentions over 1400 of the principal subjects pertaining to organic chemistry with the names of discoverers and references. To the scattered land-marks of organic chemistry before the year 1500 a page of the preface is devoted. Necessary restrictions prevented the extension of the tables after 1890. This year, with its synthesis of the sugars and other discoveries, gave such an impetus to organic research that, as Prof. Lippmann remarks, more new compounds were discovered within the next decade than in the entire preceding century. The commencement, at about this date, of abstract journals with their indexes of current literature also rendered a further continuance of the plan unnecessary.

In the selection and arrangement of his chronographic material, Prof. Lippmann has shown good judgment and impartiality. All countries, as he remarks in his introduction, have contributed their part towards erecting the temple of science and with this thought in mind he has attempted, so far as was possible, to give credit where credit was due. The following typical example will indicate his general method and fairness of treatment.

1831. Chloroform und Chloral aus Alkohol und Chlor, Liebig (*Pogg.* 24, 444; A. 1, 189; die Formeln sind noch unrichtig). Chloroform aus Alkohol und Chlorkalk, Soubeiran (A. ch. II, 48, 131); Guthrie (*Silliman's Amer. Journ.* 21, 64 (1832)); Gr. 76.

In addition to dates, compounds and authorities each page of the tables has a convenient set of footnotes that give the etymologies of the different organic chemical terms. Separate indexes of authors and subject matter assist in the work of reference.

A compendium of this character has necessarily certain shortcomings, for no two organic chemists will be found to agree in their choice of selective material. The author with full consciousness of this limitation has very modestly termed his compilation an experiment. The reviewer believes that all chemists who have occasion to consult the chronological tables of Prof. Lippmann will vote the experiment a decided success. In addition to its value as a reference booklet the work gives a general perspective of the historic development of organic chemistry such as no other volume of its size can offer.

C. A. BROWN

# THE JOURNAL

OF THE

# American Chemical Society

with which has been incorporated the

American Chemical Journal  
(Founded by Irs Remsen)

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[CONTRIBUTION FROM THE LABORATORY OF PHYSICAL CHEMISTRY OF THE ROYAL POLYTECHNICAL INSTITUTE OF COPENHAGEN]

## STUDIES ON SOLUBILITY. IV. THE PRINCIPLE OF THE SPECIFIC INTERACTION OF IONS

BY J. N. BRÖNSTED

Received June 6, 1921

### 1. Introduction

Although, according to the theory of complete dissociation of the strong electrolytes,<sup>1</sup> the thermodynamic properties of salt solutions are fairly satisfactorily accounted for by making the electrical forces arising from the net charges of the ions responsible for the deviations of such solutions from the ideal state, the total ion concentration here appearing as the predominating factor, a more detailed examination of activity coefficients, especially by means of solubility measurements,<sup>2</sup> has shown the activity of ions to depend very markedly on their individual natures and also to be distinctively influenced by the natures of the salt solutions serving as solvents. It seems to the writer, therefore, that further progress in this field can be expected only by a thorough study of those individual properties of the ions.

In recent papers MacInnes<sup>3</sup> and Harned<sup>4</sup> have made interesting contributions to the question of the activities of separate ions. The first prin-

<sup>1</sup> For literature see the first article of this series, *THIS JOURNAL*, 42, 761 (1920).

<sup>2</sup> Brönsted and Agnes Petersen, *ibid.*, 43, 2265 (1921).

<sup>3</sup> MacInnes, *ibid.*, 41, 1086 (1919).

<sup>4</sup> Harned, *ibid.*, 42, 1808 (1920).

ciples introduced by MacInnes that the activities of the cation and anion in the same solution may differ from one another does not conflict with previous views because the assumption of equality of the activity coefficients has been used only as a conscious approximation in order to simplify the question in hand. The second principle, that the activity of the chloride ion, at any given concentration, is independent of the cation associated with it, and especially the more generalized form of this principle suggested by Harned is, however, of much more questionable nature.

This principle stated by the authors as "the principle of the independent activity coefficients of the ions" involves the necessity that any ion dissolved in slight amounts in various dilute salt solutions of the same concentration should possess the same activity coefficient independent of the nature of the solvent. This, however, cannot be true because the solubility of a slightly soluble salt varies largely when passing from one solvent to another. Measurements made in this laboratory show the departure for a uni-univalent salt into uni-univalent solvents to amount in many cases to 10% in 0.1 *N* solutions. Of course if the concentration decreases, this departure will likewise decrease, but only for the reason that activity coefficients with decreasing concentration generally approach the same ideal value. It is a consequence of the results referred to above, that the activity coefficient of an ion is to a similar extent a function of the nature of this ion itself and of the solvent containing it.

The incorrectness of the principle, however, is brought out most strikingly by the following thermodynamic reasoning.

In a mixture of  $n_1, n_2, n_3, \dots$  molecules with the activities  $\xi_1, \xi_2, \xi_3, \dots$  and the activity coefficients  $f_1, f_2, f_3, \dots$  the equation

$$\sum n_i d \ln \xi_i = \sum n_i d \ln \frac{n_i}{n} + \sum n_i d \ln f_i = 0$$

holds thermodynamically,<sup>5</sup>  $n$  being the total number of molecules, and is easily reduced to

$$\sum n_i d \ln f_i = 0$$

This equation shows that when a dilute salt solution is gradually changed into another salt solution of the same concentration and the activity coefficients of the ions, according to the principle, remain constant, the same will be the case with the activity of the solvent. All salt solutions of the same concentration must, therefore, have the same freezing point, involving again the same activity coefficient for all ions, independent of their nature. The principle of the independent activity coefficients, therefore, ends in the assumption of equal activity coefficients for all ions in dilute solutions. This thermodynamic result shows clearly that this

<sup>5</sup> See Section 8 of this paper.

principle cannot be true and that it indeed contradicts the first of the above principles.<sup>6</sup>

The principle of the independent activity coefficients is based on a conjectured relation between activity and electrical conductivity of ions. Without going into details respecting the availability of such a relation, the present writer wishes to emphasize the advantage of making thermodynamically related phenomena such as freezing points, solubilities and electromotive forces a basis for calculations of activity and osmotic coefficients. By associating experimental results from these various fields of investigation, it seems to be possible to reach a more detailed survey of the thermodynamic properties of solutions, particularly as regards the problem of the mutual electrical interaction of the ions and their salting-out effect.

The possibility of interpreting the properties of salt solutions from this point of view has already been touched in the first article of this series. The object of the present paper is to prove that the activity coefficient of an ion is made up of several factors, depending partly upon properties belonging to the medium, and partly upon an interaction between the ion concerned and the ions of the solvent; and it will show, moreover, that simple means are available for determining experimentally the ratio between these separate coefficients.

This problem is most simply attacked by confining ourselves to a consideration of solutions in which the total ion concentration is kept constant so that no change in the primary Milner-effect will confuse the pic-

<sup>6</sup> In a recent interesting paper Lewis and Randall [*THIS JOURNAL*, 43, 1112 (1921)] have given a complete treatment of the theory of ion activities, in which the principle here in question is accepted and extended by introducing a new conception, the ionic strength. In spite of the obvious importance to be attached to the results resting upon the application of this conception, the conclusions of these authors as regards the problem here at hand are hardly compatible with the extensive amount of experimental material now available. It does not agree for instance with the fact found by Brönsted and Agnes Petersen (Ref. 2) that in the case of polyvalent ions the electric type is of marked influence upon the solubility. It seems as if this inconsistency may at least partly arise from the fact that the solubility of rather soluble salts was made a basis of the conclusions. Evaluating solubility data for activity determination in various solvents is possible only in a region of somewhat higher concentration than that corresponding to the solubility of the saturating salt in pure water. In the case of thallous chloride, for instance, the solubility of which is 0.016 in pure water, the apparent steep convergence of the curves corresponding to the various solvents [Lewis and Randall, *loc. cit.*, p. 1134, Fig. 4] does not involve a similar disappearance of the individualities of the solvents, but simply indicates the gradual approach of the composition of the saturated solutions to pure thallous chloride solutions. If a much less soluble modification of TlCl could be employed we should certainly find appreciable differences at 0.016 *N* concentration. Not too much weight, therefore, can be given to the complete agreement of the low concentration data extrapolated in Table XIX. The above mentioned thermodynamic argument applies of course invariably in the case of the generalized principles.



ture of the changing peculiarities. On the other hand a thorough treatment of this problem must include the effect of changing concentration as well. In this respect the chief object will be to represent the peculiarities in such a form that they will vanish uniformly as the concentration approaches zero. This question of the concentration effect will, however, be reserved for a following article.

## 2. The Complex Nature of the Activity Coefficients

In the third article of this series<sup>7</sup> a great number of examples showed that equally strong solutions of various uni-univalent salts dissolve slightly soluble metal-ammonia salts in largely varying proportions. For instance, in the case of oxalo-tetrammine cobaltic tetranitro-diammine cobaltiate the following solubilities,  $s$ , were found at 0°.

Solvent 0.1 N	$s$	Solvent 0.1 N	$s$
Na formate	0.00128	K chloride	0.00137
K formate	0.00132	K nitrate	0.00141

The first and the last numbers differ by about 10%.

The simplest way to account for such diversities would be to ascribe them to a certain dissolving power peculiar to each solvent, analogous to what has been assumed in the case of non-electrolytes dissolved in solutions of various salts. It is obvious, however, that conditions as simple as these do not prevail in the case of dissolved ions, because dissolving powers calculated in this way vary pronouncedly from one saturating salt to another.

This is shown by a good many data in the paper cited above.<sup>7</sup> It also appears clearly from the fact that the solubilities of various sparingly soluble salts are influenced quite differently by the same solvent as exhibited, for example, by the following data for oxalo-tetrammine cobaltic tetranitro-diammine cobaltiate (Ox-N) and cesium tetrathiocyanato-diammine chromiate (Cs-R) at 20°.

	$s_0$	$s$	$s/s_0$
Ox-N	0.00266	0.00372	1.40
Cs-R	0.00263	0.00323	1.23

$s_0$  and  $s$  here indicating the solubility in pure water and 0.1 N potassium nitrate solution, respectively. In spite of the nearly identical values of the solubilities of these two salts in water the solubilities in 0.1 N potassium nitrate solutions differ largely.

These facts forced us to assume certain effects of interaction between the ions in addition to the effect of the dissolving power or salting-out effect, peculiar to each salt solution. We must again assume both of these effects to result from isolated causes due to the two ions constituting

<sup>7</sup> THIS JOURNAL, 43, 2265 (1921).

the solvent salt. We must, therefore, represent the activity coefficient of a dissolved ion as a product of 4 separate coefficients, namely 2 coefficients of interaction and 2 salting-out coefficients.

In order to give these ideas a mathematical form the following notations will be used.

$f$ ,	Activity coefficients in general.
$f_K$ ,	Activity coefficients of the ion $K^+$ in general.
$f_{K(NaCl)}$ ,	Activity coefficients of the ion $K^+$ in NaCl solution.
$f_i$ ,	Coefficients of interaction in general.
$f_{K(Na)}$ ,	Coefficients of interaction of the ion $K^+$ influenced by $Na^+$ .
$f_{K(Cl)}$ ,	Coefficients of interaction of the ion $K^+$ influenced by $Cl^-$ .
$f_u$ ,	Salting-out coefficients in general.
$f_{(K)}$ ,	Salting-out coefficients of the ion $K^+$ .
$r_f$ ,	Ratio of activity coefficients in general.
$r_i$ ,	Ratio of coefficients of interaction.
$r_u$ ,	Ratio of salting-out coefficients.

Furthermore we put  $\frac{f_{K(NaCl)}}{f_{K(LiCl)}} = r_{K(NaCl/LiCl)}$ ;  $\frac{f_{K(Cl)}}{f_{K(NO_3)}} = r_{K(Cl/NO_3)}$ ;  $\frac{f_{(K)}}{f_{(Na)}} = r_{(K/Na)}$ .

By  $K$ ,  $Na$  . . . and  $Cl$ ,  $NO_3$  . . . is here meant not only potassium, sodium . . . chloride and nitrate ions but generally various cations and anions respectively.

By means of the above assumption regarding the complex nature of the activity coefficient we can, for example, express the activity coefficient for the potassium ions as follows.

$$f_{K(NaCl)} = f_{K(Na)} f_{K(Cl)} f_{(Na)} f_{(Cl)} \quad (1)$$

While the coefficient of interaction is determined by the nature of the ions of both the solute and the solvent salt, the salting-out coefficient obviously has a more general character, as it depends merely upon the solvent itself.

### 3. The Principle of the Specific Interaction of Ions

Various considerations have led the writer to conclude that the above expression (1) for the activity coefficient of an ion can be largely simplified, namely, by introducing what we shall call the *principle of the specific interaction of ions*. This principle may be stated as follows.

*In a dilute salt solution of constant total concentration, ions will be uniformly influenced by ions of their own sign.*

We can therefore write

$$f_{K(K)} = f_{K(Na)} = f_{Cl(Cl)} = f_{Cl(NO_3)} = k \quad (2)$$

$k$  being a constant depending only upon the concentration. For the present purpose, when we are comparing solutions of the same concentration, it can be equated to unity. We then obtain the following fundamental equations as a complete statement of our principles.

$$\left. \begin{aligned} f_{K(KCl)} &= f_{K(Cl)} f_{(K)} f_{(Cl)} \\ f_{K(NaCl)} &= f_{K(Cl)} f_{(Na)} f_{(Cl)} \end{aligned} \right\} \quad (3)$$

That this simplification is allowable becomes probable from a theoretical point of view when we remember that the individual deviations of salts in dilute solutions are mainly due to secondary electric forces<sup>8</sup> determined by the size and structure of the ions and the number and positions of the separate electric charges of which the net charge is composed. In the case of ions of the same sign the repelling forces will tend to keep them apart and therefore, in dilute solution, to annihilate secondary effects perceptible only when the ions have sufficiently approached to one another.

Experimental indications of the validity of the above principle are furnished by electrical measurements<sup>9</sup> concerning the activity coefficient of the chlorine ion in 0.1 *N* potassium chloride and potassium nitrate solutions. In spite of the chloride dissolving, on an average, about 4% less of slightly soluble salts than the nitrate, the activity coefficient of the chloride ion by means of these measurements was found to be only 1% higher in the chloride than in the nitrate solutions. From this result we draw the inference that the activity coefficients of anions vary very little when passed from one solution to another having the same cation. From these observations the above principle may be derived as a probable conclusion.

For fully establishing the principle, however, the simplest and the most direct way would be to utilize solubility data furnished by slightly soluble salts in salt solutions as solvents. It is the object of the following discussion to present the results achievable from such an examination and to show the conclusions they are leading to for the theory of solutions in general.

#### 4. Introduction of the Theory of the Complex Nature of the Activity Coefficients and of the Principle of the Specific Interaction of Ions in the Theory of Solubility of Salts in Hetero-ionic Salt Solutions

In no other field are the individualities of salt solutions more pronouncedly exhibited than in the field of solubility of sparingly soluble salts in solutions of other salts as solvents. According to our theory these individualities are due partly to a peculiar avidity between ions of opposite sign represented by the coefficients of interaction, partly to a specific dissolving power exerted by the ions of the solvent and represented by the salting-out coefficients.

In order to avoid too much abstraction and complicated notations the principles stated above will be introduced by using, as far as possible, the symbols of well-known salts to represent the various types.

<sup>8</sup> Brönsted, *THIS JOURNAL*, **42**, 781 (1920).

<sup>9</sup> Brönsted, *K. Danske Vid. Selsk. Mat.-fys. Med.*, **3**, No. 9 (1920).

Thus, for instance, by  $\text{AgCl}$  and  $\text{PbCl}_2$  we shall denote uni-univalent and unibivalent salts with a common anion; by  $\text{KCl}$  and  $\text{KNO}_3$ , salts having a cation in common, etc.

Let  $s_{\text{AgCl}}$ ,  $P_{\text{AgCl}}$  and  $\Pi_{\text{AgCl}}$  stand for solubility, stoichiometric solubility product and thermodynamic solubility product, respectively, of  $\text{AgCl}$ ; then using for the activity coefficients the notation suggested in the foregoing section we can write in the case of a potassium nitrate solution saturated with  $\text{AgCl}$ ,

$$\Pi_{\text{AgCl}} = P_{\text{AgCl}} f_{\text{Ag}(\text{KNO}_3)} f_{\text{Cl}(\text{KNO}_3)} \quad (4)$$

or introducing our principles by means of

$$\left. \begin{aligned} f_{\text{Ag}(\text{KNO}_3)} &= f_{\text{Ag}(\text{NO}_3)} f_{\text{(K)}} f_{\text{(NO}_3)} \\ f_{\text{Cl}(\text{KNO}_3)} &= f_{\text{Cl}(\text{K)}} f_{\text{(K)}} f_{\text{(NO}_3)} \end{aligned} \right\} \quad (5)$$

the following equation,

$$\Pi_{\text{AgCl}} = s_{\text{AgCl}}^2(\text{KNO}_3) f_{\text{Ag}(\text{NO}_3)} f_{\text{Cl}(\text{K)}} f_{\text{(K)}}^2 f_{\text{(NO}_3)}^2 \quad (6)$$

In the case of an equally strong sodium nitrate solution as solvent we obtain analogously

$$\Pi_{\text{AgCl}} = s_{\text{AgCl}}^2(\text{NaNO}_3) f_{\text{Ag}(\text{NO}_3)} f_{\text{Cl}(\text{Na)}} f_{\text{(Na)}}^2 f_{\text{(NO}_3)}^2 \quad (7)$$

and combining (6) and (7)

$$\frac{s_{\text{AgCl}}(\text{KNO}_3)}{s_{\text{AgCl}}(\text{NaNO}_3)} = \left( \frac{f_{\text{Cl}(\text{Na)}}}{f_{\text{Cl}(\text{K)}}} \right)^{1/2} \frac{f_{\text{(Na)}}}{f_{\text{(K)}}} \quad (8)$$

which by means of (5) can be rewritten as follows.

$$\frac{s_{\text{AgCl}}(\text{KNO}_3)}{s_{\text{AgCl}}(\text{NaNO}_3)} = \left( \frac{f_{\text{Cl}(\text{NaNO}_3)}}{f_{\text{Cl}(\text{KNO}_3)}} \right)^{1/2} \left( \frac{f_{\text{(Na)}}}{f_{\text{(K)}}} \right)^{1/2} \quad (9)$$

Introducing for the solubility ratio the symbol  $R$  and also the  $r$  from Section 2 (above), by means of

$$\frac{s_{\text{AgCl}}(\text{KNO}_3)}{s_{\text{AgCl}}(\text{NaNO}_3)} = R_{\text{AgCl}(\text{KNO}_3/\text{NaNO}_3)} \quad (10)$$

Equations 8 and 9 are transformed into

$$R_{\text{AgCl}(\text{KNO}_3/\text{NaNO}_3)} = r^{1/2}_{\text{Cl}(\text{Na}/\text{K})} r_{\text{(Na)/K}} \quad (11)$$

$$R_{\text{AgCl}(\text{KNO}_3/\text{NaNO}_3)} = r^{1/2}_{\text{Cl}(\text{NaNO}_3/\text{KNO}_3)} r^{1/2}_{\text{(Na)/K}} \quad (12)$$

Since the coefficients belonging to the silver and nitrate ions do not enter into these equations we are obviously justified in making the following deduction, that *when using as solvents equally strong solutions with an anion in common the solubility ratio shown by a slightly soluble uni-univalent and hetero-ionic salt depends only on the anion of the saturating salt and the cations of the two solvents.* According to this theory we shall therefore find, for instance,

$$\frac{s_{\text{AgCl}}(\text{KNO}_3)}{s_{\text{AgCl}}(\text{NaNO}_3)} = \frac{s_{\text{AgCl}}(\text{KClO}_3)}{s_{\text{AgCl}}(\text{NaClO}_3)} = \frac{s_{\text{TiCl}}(\text{KNO}_3)}{s_{\text{TiCl}}(\text{NaNO}_3)}$$

As an analogous rule it is evident that when the two solvents possess a common cation we can also write

$$\frac{s_{\text{AgCl}(\text{KNO}_3)}}{s_{\text{AgCl}(\text{KClO}_3)}} = \left( \frac{f_{\text{Ag}(\text{ClO}_3)}}{f_{\text{Ag}(\text{NO}_3)}} \right)^{1/2} \frac{f_{\text{ClO}_3}}{f_{\text{NO}_3}} = \left( \frac{f_{\text{Ag}(\text{KClO}_3)}}{f_{\text{Ag}(\text{KNO}_3)}} \right)^{1/2} \left( \frac{f_{\text{ClO}_3}}{f_{\text{NO}_3}} \right)^{1/2}$$

or

$$\frac{s_{\text{AgCl}(\text{KNO}_3)}}{s_{\text{AgCl}(\text{KClO}_3)}} = \frac{s_{\text{AgCl}(\text{NaNO}_3)}}{s_{\text{AgCl}(\text{NaClO}_3)}} = \frac{s_{\text{AgClO}_3(\text{KNO}_3)}}{s_{\text{AgClO}_3(\text{KClO}_3)}}$$

It is not difficult to extend these results to cases in which the saturating salt is of a higher type. If we consider luteo cobaltic chromate, for instance, the symbol of which is  $\text{L}_2(\text{CrO}_4)_2$  (L standing for the luteo ion  $\text{Co}(\text{NH}_3)_6$ ) the following equations are obtained.

$$\left. \begin{aligned} \frac{s_{\text{L}_2(\text{CrO}_4)_2(\text{KNO}_3)}}{s_{\text{L}_2(\text{CrO}_4)_2(\text{NaNO}_3)}} &= \left( \frac{f_{\text{CrO}_4(\text{Na})}}{f_{\text{CrO}_4(\text{K})}} \right)^{1/2} \frac{f_{\text{Na}}}{f_{\text{K}}} \\ \frac{s_{\text{L}_2(\text{CrO}_4)_2(\text{KNO}_3)}}{s_{\text{L}_2(\text{CrO}_4)_2(\text{NaNO}_3)}} &= \left( \frac{f_{\text{CrO}_4(\text{NaNO}_3)}}{f_{\text{CrO}_4(\text{KNO}_3)}} \right)^{1/2} \left( \frac{f_{\text{Na}}}{f_{\text{K}}} \right)^{1/2} \\ \frac{s_{\text{L}_2(\text{CrO}_4)_2(\text{KNO}_3)}}{s_{\text{L}_2(\text{CrO}_4)_2(\text{KCl})}} &= \left( \frac{f_{\text{L}(\text{Cl})}}{f_{\text{L}(\text{NO}_3)}} \right)^{1/2} \frac{f_{\text{Cl}}}{f_{\text{NO}_3}} \\ \frac{s_{\text{L}_2(\text{CrO}_4)_2(\text{KNO}_3)}}{s_{\text{L}_2(\text{CrO}_4)_2(\text{KCl})}} &= \left( \frac{f_{\text{L}(\text{KCl})}}{f_{\text{L}(\text{KNO}_3)}} \right)^{1/2} \left( \frac{f_{\text{Cl}}}{f_{\text{NO}_3}} \right)^{1/2} \end{aligned} \right\} \quad (13)$$

or

$$\left. \begin{aligned} R_{\text{L}_2(\text{CrO}_4)_2(\text{KNO}_3/\text{NaNO}_3)} &= r^{2/2} \text{CrO}_4(\text{Na}/\text{K}) \quad r_{\text{Na}/\text{K}} \\ R_{\text{L}_2(\text{CrO}_4)_2(\text{KNO}_3/\text{NaNO}_3)} &= r^{1/2} \text{CrO}_4(\text{NaNO}_3/\text{KNO}_3) \quad r^{1/2}(\text{Na}/\text{K}) \\ R_{\text{L}_2(\text{CrO}_4)_2(\text{KNO}_3/\text{KCl})} &= r^{1/2} \text{L}(\text{Cl}/\text{NO}_3) \quad r_{\text{Cl}/\text{NO}_3} \\ R_{\text{L}_2(\text{CrO}_4)_2(\text{KNO}_3/\text{KCl})} &= r^{1/2} \text{L}(\text{KCl}/\text{KNO}_3) \quad r^{1/2}(\text{Cl}/\text{NO}_3) \end{aligned} \right\} \quad (14)$$

From the form of these equations we learn that the above rule for univalent saturating salts holds true also when saturating salts of higher types are employed. The solubility ratio is obviously independent of the common ion of the solvents and also of the nature of the ion of opposite sign in the saturating salt as far as saturating salts of the same type are considered. It is very important to note, however, that the form of the equations varies with the type of the saturating salt, as this fact enables us to compute the values of  $r_i$  and  $r_s$  separately.

We carry out this calculation preferably by means of a special example, applying for instance Equation 16 to the three salts (1) oxalo-tetrammine cobaltic tetranitro-diammine cobaltate (symbol  $\text{OxN}$ ),  $[\text{Co}(\text{NH}_3)_4\text{C}_2\text{O}_4] [\text{Co}(\text{NH}_3)_2(\text{NO}_2)_4]$ , (2) xantho cobaltic tetranitro-diammine cobaltate (symbol  $\text{XN}_2$ ),  $[\text{Co}(\text{NH}_3)_6\text{NO}_2] [\text{Co}(\text{NH}_3)_2(\text{NO}_2)_4]$ , and (3) luteo cobaltic tetranitro-diammine cobaltate ( $\text{LN}_2$ ),  $[\text{Co}(\text{NH}_3)_6] [\text{Co}(\text{NH}_3)_2(\text{NO}_2)_4]$ , each containing the same univalent anion and a uni-, bi- and trivalent cation, respectively. Application of Equation 16 gives in the three cases

for the solubility ratio  $R$ , using potassium and sodium nitrates as solvents,

$$R_I = R_{OxN(KNO_3/NaNO_3)} = r^{1/2}_{N(Na/K)} r_{(Na/K)} \quad (15)$$

$$R_{II} = R_{KN_2(KNO_3/NaNO_3)} = r^{2/3}_{N(Na/K)} r_{(Na/K)} \quad (16)$$

$$R_{III} = R_{LN_3(KNO_3/NaNO_3)} = r^{3/4}_{N(Na/K)} r_{(Na/K)} \quad (17)$$

From two of these equations the ratio of interaction  $r_{N(Na/K)}$  and the salting-out ratio  $r_{(Na/K)}$  can obviously be determined by means of the experimentally found solubility ratios  $R_I$ ,  $R_{II}$  and  $R_{III}$ . For the ratio of interaction we obtain

$$r_i = r_{N(Na/K)} = \left(\frac{R_{II}}{R_I}\right)^4 = \left(\frac{R_{III}}{R_I}\right)^{12} = \left(\frac{R_{III}}{R_{II}}\right)^{12}; \quad (18)$$

and for the salting-out ratio,

$$r_u = r_{(Na/K)} = \frac{R_I^4}{R_{II}^3} = \frac{R_I^3}{R_{III}^2} = \frac{R_{II}^9}{R_{III}^8} \quad (19)$$

showing the ratios  $R_I$ ,  $R_{II}$  and  $R_{III}$  to be correlated also.

According to Equation 3 the ratio of the two activity coefficients  $r_f = \frac{f_{N(NaNO_3)}}{f_{N(KNO_3)}}$  is given by

$$r_f = r_i r_u \quad (19a)$$

and is thus determinable from the same solubility ratios.

Corresponding results are easily obtained when other types of saturating salts are considered.

In these equations our principles have been given such a form that they can be subjected to a direct experimental test.

It may be expected, perhaps, that the  $r_u$  value derivable by means of Equation 24 or analogous equations would obtain also in the case of non-electrolytes, a saturating substance here representing directly the solubility ratio. This would indeed be the case if no interaction between ions and neutral molecules occurred. According to H. v. Euler<sup>10</sup> neutral substances in many cases exhibit the same solubility ratio in two solvents, a fact which is found consistent with the above assumption. Further inquiry in this field, however, shows deviations to exist, which in certain cases are very considerable, and it is therefore necessary to assume a kind of interaction between ions and *neutral molecules*. This, however, is generally slight, compared with the action between ions of opposite sign.

When utilizing argon or another inert gas as saturating substance any peculiar interaction would probably be precluded, and we should therefore expect the ratio of solubility of such a substance in two salt solutions to be identical with the  $r_u$  for these solvents found in the way described.

<sup>10</sup> Euler, *Z. physik. Chem.*, 31, 360 (1899); *Z. Elektrochem.*, 23, 192 (1917).

### 5. Experiments Covering Solubilities in Hetero-ionic Solvents

**Experiment of Minor Accuracy.**—Most of the experimental material referred to in this section was produced for other purposes than that of verifying the above principles, and it is but moderately accurate.

In the first place, experiments were available utilizing certain xantho cobaltic and chloro-pentammine cobaltic salts, namely:

Xantho cobaltic tetrathiocyanato-diammine chromiate.....	(XR <sub>2</sub> )
Xantho cobaltic tetranitro-diammine cobaltiate.....	(XN <sub>2</sub> )
Chloro-pentammine cobaltic tetrathiocyanato-diammine chromiate.....	(PR <sub>2</sub> )
Chloro-pentammine cobaltic tetranitro-diammine cobaltiate.....	(PN <sub>2</sub> )

using uni-univalent salt solutions as solvents. The results are given in Tables I and II. The figures here and in the following tables represent mols. per liter of the solution.

TABLE I  
SOLUBILITY OF XR<sub>2</sub> AND XN<sub>2</sub> IN 0.2 M SALT SOLUTIONS AT 0° AND 20°

Solvent	XR <sub>2</sub> , <i>t</i> = 0° × 10 <sup>4</sup>	XR <sub>2</sub> , <i>t</i> = 20° × 10 <sup>4</sup>	XN <sub>2</sub> , <i>t</i> = 0° × 10 <sup>4</sup>	XN <sub>2</sub> , <i>t</i> = 20° × 10 <sup>4</sup>
H <sub>2</sub> O	392	1284	311	992
NaCHO <sub>2</sub>	629	1950	570	1692
KCHO <sub>2</sub>	667	2040	629	1824
NaCl	680	2097	621	1823
KCl	723	2193	682	1952
NaNO <sub>3</sub>	746	2228	...	....
KNO <sub>3</sub>	790	2325	...	....

TABLE II  
SOLUBILITY OF PR<sub>2</sub> AND PN<sub>2</sub> IN 0.2 M SALT SOLUTIONS AT 0° AND 20°

Solvent	PR <sub>2</sub> , <i>t</i> = 0° × 10 <sup>4</sup>	PR <sub>2</sub> , 20° × 10 <sup>4</sup>	PN <sub>2</sub> , <i>t</i> = 0° × 10 <sup>4</sup>	PN <sub>2</sub> , <i>t</i> = 20° × 10 <sup>4</sup>
H <sub>2</sub> O	...	...	173	637
NaCHO <sub>2</sub>	477	1516	325	1100
KCHO <sub>2</sub>	510	1592	363	1207
NaCl	524	1627	353	1187
KCl	548	1702	393	1291

By means of these figures the solubility ratios have been calculated and are collected in Table III.

TABLE III  
RATIOS OF SOLUBILITY OF XR<sub>2</sub>, XN<sub>2</sub>, PR<sub>2</sub> AND PN<sub>2</sub> IN VARIOUS 0.2 M SOLVENTS

Solvent	<i>t</i> = 0°		<i>t</i> = 20°	
	XR <sub>2</sub>	PR <sub>2</sub>	XR <sub>2</sub>	PR <sub>2</sub>
KCHO <sub>2</sub> /NaCHO <sub>2</sub>	1.060	1.069	1.046	1.050
KCl/NaCl	1.063	1.046	1.046	1.046
KNO <sub>3</sub> /NaNO <sub>3</sub>	1.059	1.046	1.044	1.046
K <sup>+</sup> /Na <sup>+</sup> , mean	1.059		1.046	
	XN <sub>2</sub>	PN <sub>2</sub>	XN <sub>2</sub>	PN <sub>2</sub>
KCHO <sub>2</sub> /NaCHO <sub>2</sub>	1.103	1.119	1.078	1.097
KCl/NaCl	1.098	1.115	1.071	1.088
K <sup>+</sup> /Na <sup>+</sup> , mean	1.109		1.084	

	$XR_2$	$XN_2$	$XR_2$	$XN_2$
NaCl/NaCHO <sub>2</sub>	1.081	1.090	1.076	1.077
KCl/KCHO <sub>2</sub>	1.083	1.087	1.075	1.070
Cl <sup>-</sup> /CHO <sub>2</sub> <sup>-</sup> , mean	1.085		1.075	
	$XR_2$		$XR_2$	
NaNO <sub>2</sub> /NaCHO <sub>2</sub>	1.186		1.143	
KNO <sub>2</sub> /KCHO <sub>2</sub>	1.183		1.140	
NO <sub>2</sub> <sup>-</sup> /CHO <sub>2</sub> <sup>-</sup> , mean	1.184		1.142	
	$PR_2$	$PN_2$	$PR_2$	$PN_2$
NaCl/NaCHO <sub>2</sub>	1.098	1.086	1.073	1.079
KCl/KCHO <sub>2</sub>	1.074	1.084	1.071	1.070
Cl <sup>-</sup> /CHO <sub>2</sub> <sup>-</sup> , mean	1.086		1.073	

The figures in this table furnish a good verification of the principle of the specific interaction of the ions. The agreement of the figures within each group in the tables shows that the action between ions of the same sign hardly surmounts the possible experimental error. The results may be stated in the following way by means of Equation 14.

TABLE IV

	$t = 0^\circ$	$t = 20^\circ$
$r^{1/2}_R(Na/K) \quad r(Na/K)$	1.059	1.046
$r^{1/2}_N(Na/K) \quad r(Na/K)$	1.109	1.084
$r^{1/2}_X(HCOO/Cl) \quad r(HCOO/Cl)$	1.085	1.075
$r^{1/2}_X(HCOO/NO_2) \quad r(HCOO/NO_2)$	1.184	1.142
$r^{1/2}_P(HCOO/Cl) \quad r(HCOO/Cl)$	1.086	1.073

These figures show that the coefficients of interaction may differ very markedly from one another. The relative action of Na<sup>+</sup> and K<sup>+</sup> is thus seen to be about 7% higher for the N<sup>-</sup> than for the R<sup>-</sup> ion. The  $r$ -coefficients themselves cannot be calculated from these figures since salts of only a single type are employed as saturating salts. With the rise of temperature the peculiarity diminishes and the ratios approach unity.

In the following tables are the results of some further experiments covering cesium tetrathiocyanato-diammine chromiate and cesium tetranitro-diammine cobaltate in various solvents.

TABLE V  
SOLUBILITY OF CsR AND CsN IN VARIOUS SOLVENTS AT 0°

<i>M</i>	Solvent	CsR × 10 <sup>6</sup>	CsN × 10 <sup>6</sup>
	H <sub>2</sub> O	789	532
1.0	NaCHO <sub>2</sub>	831	785
1.0	NaNO <sub>2</sub>	1365	1268
0.5	Mg(NO <sub>2</sub> ) <sub>2</sub>	1356	1113
0.5	MgSO <sub>4</sub>	973	815



TABLE VI  
RATIOS OF SOLUBILITY OF CsR AND CsN IN SOLVENTS AT 0°

Solvent	CsR	CsN	Mean
NaNO <sub>2</sub> /NaCHO <sub>2</sub>	1.64	1.62	1.63
Mg(NO <sub>3</sub> ) <sub>2</sub> /MgSO <sub>4</sub>	1.39	1.37	1.38
NaNO <sub>2</sub> /Mg(NO <sub>3</sub> ) <sub>2</sub>	1.01	1.14	...

The agreement found here between the ratios in solvents with a common cation and the disagreement between the ratios in solvents with a common anion verify closely the rule of the specific action of the ions and the absence of any action between ions of the same sign. This is the more remarkable as in this case the increase in solubility is very high on account of the high concentration of the solvents employed.

The results of a series of measurements covering the four salts cesium tetrathiocyanato chromiate (CsR), cesium tetranitro cobaltiate (CsN) and the corresponding oxalo-tetrammine cobaltic salts (OxR and OxN) in which nitrates and chlorides of potassium and sodium were employed as solvents, are tabulated below.

TABLE VII  
SOLUBILITY OF CsN, OxN, CsR AND OxR IN 0.1M SALT SOLUTIONS AT 20°

Solvent	CsN × 10 <sup>4</sup>	OxN × 10 <sup>4</sup>	CsR × 10 <sup>4</sup>	OxR × 10 <sup>4</sup>
H <sub>2</sub> O	17130	2659	2629	1366
KNO <sub>3</sub>	20920	3723	3233	1813
NaNO <sub>2</sub>	20550	3615	3182	1786
KCl	20210	3647	3110	1771
NaCl	19870	3531	3072	1737

TABLE VIII  
SOLUBILITY RATIOS OF CsN, CsR, OxN AND OxR IN 0.1M. SOLUTIONS OF ALKALI NITRATES AND CHLORIDES, AND WATER AT 20°

Solvent	CsN	OxN	CsR	OxR
KNO <sub>3</sub>	1.222	1.400	1.230	1.327
NaNO <sub>2</sub>	1.200	1.360	1.210	1.307
KCl	1.180	1.372	1.183	1.296
NaCl	1.162	1.328	1.168	1.271

TABLE IX  
SOLUBILITY RATIOS OF CsN, OxN, CsR AND OxR IN ALKALI NITRATES AND CHLORIDES AT 20°

Solvents	CsN	CsR	
KNO <sub>3</sub> /KCL	1.036	1.040	
NaNO <sub>2</sub> /NaCl	1.033	1.036	$r^{1/2}_{Cs(Cl/NO_2)} \quad r_{(Cl/NO_2)} = 1.036$
	OxN	OxR	
KNO <sub>3</sub> /KCl	1.021	1.024	$r^{1/2}_{Ox(Cl/NO_2)} \quad r_{(Cl/NO_2)} = 1.024$
NaNO <sub>2</sub> /NaCl	1.024	1.028	
	CsN	OxN	$r^{1/2}_{N(Na/K)} \quad r_{(Na/K)} = 1.030$
KNO <sub>3</sub> /NaNO <sub>2</sub>	(1.018)	1.030	
KCl/NaCl	(1.016)	1.030	$r^{1/2}_{R(Na/K)} \quad r_{(Na/K)} = 1.016$
	CsR	OxR	
KNO <sub>3</sub> /NaNO <sub>2</sub>	1.017	1.015	
KCl/NaCl	1.013	1.019	

The two numbers in parentheses are evidently too low, perhaps due to the fact that the solid cesium tetranitro cobaltate takes up some potassium salt from the solution to form a solid mixture. Such a behavior may be expected because the crystals are very similar, certainly isomorphic, and the solubility is of the same order of magnitude. This, however, will not interfere with the other values if, as we must assume, potassium nitrate and potassium chloride behave uniformly. In the case of the corresponding tetrathiocyanato chromiates an analogous phenomenon is precluded by the widely differing solubilities of the potassium and cesium salts of this anion.<sup>11</sup>

Otherwise, as shown by Table X, the agreement between the figures in each group justifies the conclusion that in this case also we have a good verification of the principles to be tested.

Finally, we may add the results of some measurements with praseo salts.

As the purity of these salts could not be tested in the usual way on account of their instability the data in question are of minor value. Still, a conclusion confirming our principle may be drawn from them.  $\text{Pi}^-$  indicates the picrate ion and  $\text{Rh}^-$  the thiocyanate ion.

TABLE X  
SOLUBILITY OF PRASEO SALTS IN VARIOUS SOLVENTS AT 0°

Solvent <i>M</i>	$\text{PrRh}$ $\times 10^4$	$\text{PrNO}_2$ $\times 10^4$	$\text{PrIO}_3$ $\times 10^4$	$\text{PrPi}$ $\times 10^4$
0.1 KCl	3580	5000	5710	295
0.1 NaCl	3530	4835	5680	285.5
0.1 $\text{KClO}_3$	3645	....	5790	....
0.1 $\text{NaClO}_3$	3605	....	5760	....
0.05 KCl	3355	5480	5250	274
0.05 NaCl	3320	4510	5240	266
0.05 $\text{KClO}_3$	3390	....	5310	...
0.05 $\text{NaClO}_3$	3370	....	5280	...
$\text{H}_2\text{O}$	2820	3860	4410	212

TABLE XI  
RATIOS OF SOLUBILITY OF PRASEO SALTS IN 0.1 *M* ALKALI CHLORIDES AND CHLORATES  
AT 0°

Solvents	$\text{PrRh}$	$\text{PrIO}_3$		
$\text{KClO}_3/\text{KCl}$	1.017	1.013	$r^{1/2}_{\text{Pr}(\text{Cl}/\text{ClO}_3)} r_{(\text{Cl}/\text{ClO}_3)}$	= 1.016
$\text{NaClO}_3/\text{NaCl}$	1.021	1.013		
$\text{KCl}/\text{NaCl}$	1.014	}	$r^{1/2}_{\text{Rh}(\text{Na}/\text{K})} r_{(\text{Na}/\text{K})}$	= 1.011
$\text{KClO}_3/\text{NaClO}_3$	1.008			
$\text{KCl}/\text{NaCl}$	1.005	}	$r^{1/2}_{\text{IO}_3(\text{Na}/\text{K})} r_{(\text{Na}/\text{K})}$	= 1.005
$\text{KClO}_3/\text{NaClO}_3$	1.005			

<sup>11</sup> Later experiments have shown that a similar effect is still perceptible in this system. The ratios 1.017 and 1.013 in Table IX are therefore certainly somewhat too low.

The very slight difference found between the solubility of  $\text{PrIO}_3$  in  $\text{K}^+$  and  $\text{Na}^+$  solvents agrees with the fact that solutions of potassium and sodium iodates are materially alike in respect to their osmotic properties as shown by Jahn<sup>12</sup> and Hall and Harkins.<sup>13</sup> The relation here referred to between osmotic coefficients and activity is derived on the basis of our principle in Section 8.

**Experiments of Higher Accuracy.**—A series of experiments has been begun in this laboratory for the purpose of securing very accurate data for verifying our principles. All these data will be reserved for a special article. Only a few results may be stated here in order to show the accuracy obtainable and the exactness with which our principles hold.

Tenth normal solutions of potassium and sodium nitrate served as solvents. The saturating salts contained the univalent tetranitro cobaltiate anion  $\text{Co}(\text{NH}_3)_2(\text{NO}_2)_4^-$ . The cations and the corresponding solubility ratio are given in the following table.

TABLE XII  
SOLUBILITY RATIOS  $s_{\text{KNO}_3}/s_{\text{NaNO}_3}$  OF VARIOUS TETRANITRO-DIAMMINE COBALTiates AT 20°.

Cation	$s_{\text{KNO}_3}/s_{\text{NaNO}_3}$
Oxalo-tetrammine cobaltic.....	1.0339
Silver.....	1.0343
Tetramethyl-ammonium.....	1.0340
Carbonato-tetrammine cobaltic.....	1.0324
	<hr/>
$R$	= 1.0339
Chloro-pentammine cobaltic.....	1.0411
Xantho cobaltic.....	1.0414
	<hr/>
$R$	= 1.0413
Triethylene-diammine cobaltic.....	1.0450
Aquo-pentammine cobaltic.....	1.0465
	<hr/>
$R$	= 1.0458

By means of Equations 15–17 we can compute the  $R$  when introducing  $r_i = 1.0476$  and  $r_u = 1.0101$ . The  $R$  values thus calculated are given in Table XIII together with those found.

	$R$ found	$R$ calculated
$R_I$	1.0339	1.0339
$R_{II}$	1.0413	1.0419
$R_{III}$	1.0458	1.0460

The agreement leaves nothing to be desired.

<sup>12</sup> Jahn, *Z. physik. Chem.*, **59**, 37 (1907).

<sup>13</sup> Hall and Harkins, *THIS JOURNAL*, **38**, 2669 (1916).

## 6. Application of the Theory to Solutions in Homo-ionic Solvents

The solubility of a uni-univalent salt in a homo-ionic salt solution is determined by

$$\Pi_{AgCl} = P_{AgCl(KCl)} f_{Ag(K)} f_{Ag(Cl)} f_{Cl(K)} f_{Cl(Cl)} f^2_{(K)} f^2_{(Cl)} \quad (20)$$

where the same notation is used as in Section 3. Introducing the principles of the specific interaction we can write

$$\left. \begin{aligned} \Pi_{AgCl} &= P_{AgCl(KCl)} f_{Ag(Cl)} f_{Cl(K)} f^2_{(K)} f^2_{(Cl)} \\ \Pi_{AgCl} &= P_{AgCl(NaCl)} f_{Ag(Cl)} f_{Cl(Na)} f^2_{(Na)} f^2_{(Cl)} \end{aligned} \right\} \quad (21)$$

and therefore

$$\left( \frac{P_{AgCl(KCl)}}{P_{AgCl(NaCl)}} \right)^{1/2} = \left( \frac{f_{Cl(Na)}}{f_{Cl(K)}} \right) \frac{f_{(Na)}}{f_{(K)}} \quad (22)$$

Putting

$$\left( \frac{P_{AgCl(KCl)}}{P_{AgCl(NaCl)}} \right)^{1/2} = R_{AgCl(KCl/NaCl)} \quad (23)$$

and introducing the same  $r$ -coefficients as in the foregoing section we obtain,

$$R_{AgCl(KCl/NaCl)} = r^{1/2}_{Cl(Na/K)} r_{(Na/K)} = r^{1/2}_{Cl(NaCl/KCl)} r^{1/2}_{(Na/K)} \quad (24)$$

in full analogy to the corresponding Equation 12 in the case of hetero-ionic solvents.

If the saturating salt has the composition  $L_2(CrO_4)_2$  and is dissolved in the two solvents  $K_2CrO_4$  and  $Na_2CrO_4$  the following equation is obtained

$$\left( \frac{P_{L_2(CrO_4)_2(K_2CrO_4)}}{P_{L_2(CrO_4)_2(Na_2CrO_4)}} \right)^{1/4} = \left( \frac{f_{CrO_4(Na)}}{f_{CrO_4(K)}} \right) \frac{f_{(Na)}}{f_{(K)}} \quad (25)$$

or

$$R_{L_2(CrO_4)_2(K_2CrO_4/Na_2CrO_4)} = r^{3/4}_{CrO_4(Na/K)} r_{(Na/K)} = r^{3/4}_{CrO_4(Na_2CrO_4/K_2CrO_4)} r^{1/4}_{(Na/K)} \quad (26)$$

also fully analogous to the corresponding Equation 14.

The ratios of interaction and the salting-out ratios are of course determinable from Equations 25 and 26 in just the same way as from Equations 13 and 14 in the case of hetero-ionic solvents. Equations 15–19 are therefore also valid for homo-ionic solvents, the only difference being that when hetero-ionic solvents are used  $R$  represents directly the solubility ratio, (p. 892) while in the case of homo-ionic solvents as stated above it means the  $n$ th root of the ratio of solubility products,  $n$  being the total number of ions contained in one molecule of the saturating salt. As in Equations 22–26 all coefficients belong to the ions of the solvent itself; dissolution of homo-ionic solutes leads directly to a determination of the interaction of ions in the salt solutions employed as solvents.

## 7. Experiments Covering Solubilities in Homo-ionic Solvents

In order to examine the theoretical results reached in the foregoing

section a series of measurements was carried out with cobalt ammonia salts dissolved in homo-ionic solvents. The saturating salts employed contained the following complex ions: oxalo-tetrammine cobaltic, (symbol, Ox),  $[\text{Co}(\text{NH}_3)_4\text{C}_2\text{O}_4]$ ; chloro-pentammine cobaltic (symbol, [Cl]),  $[\text{Co}(\text{NH}_3)_5\text{Cl}]$ ; bromo-pentammine cobaltic, (symbol, [Br]),  $[\text{Co}(\text{NH}_3)_5\text{Br}]$ ; luteo cobaltic, (symbol, L),  $[\text{Co}(\text{NH}_3)_6]$ ; oxalo-dinitro-diammine cobaltate ion, (symbol, On),  $[\text{Co}(\text{NH}_3)_2(\text{NO}_2)_2\text{C}_2\text{O}_4]$ ; and the solvents were 0.1 *M* solutions of potassium nitrate, sodium nitrate, potassium chloride and sodium chloride. The temperature of the experiment was 0° and the same method was used as stated in an earlier communication.<sup>2</sup> The results of the measurements are given in the following tables.

TABLE XIV

SOLUBILITY OF NITRATES IN POTASSIUM NITRATE AND SODIUM NITRATE SOLUTIONS AT 0°

Saturating Salt	0.1 <i>M</i> KNO <sub>3</sub> × 10 <sup>3</sup>	0.1 <i>M</i> NaNO <sub>3</sub> × 10 <sup>3</sup>	$P_{\text{KNO}_3}/P_{\text{NaNO}_3}$	<i>R</i>
OxNO <sub>3</sub>	816	777	1.051	1.025
[Cl](NO <sub>3</sub> ) <sub>2</sub>	3970	3670	1.092	1.030
L(NO <sub>3</sub> ) <sub>2</sub>	4930	4500	1.131	1.031

TABLE XV

SOLUBILITY OF CHLORIDES IN POTASSIUM CHLORIDE AND SODIUM CHLORIDE SOLUTIONS AT 0°

Saturating Salt	0.1 <i>M</i> KCl × 10 <sup>3</sup>	0.1 <i>M</i> NaCl × 10 <sup>3</sup>	$P_{\text{KCl}}/P_{\text{NaCl}}$	<i>R</i>
OxCl	5810	5700	1.020	1.010
[Cl]Cl <sub>2</sub>	610	593	1.029	1.010
[Br]Cl <sub>2</sub>	220	213	1.033	1.008

TABLE XVI

SOLUBILITY OF KON IN POTASSIUM NITRATE AND POTASSIUM CHLORIDE SOLUTIONS AT 0°

	0.1 <i>M</i> KNO <sub>3</sub> × 10 <sup>3</sup>	0.1 <i>M</i> KCl × 10 <sup>3</sup>	$P_{\text{KNO}_3}/P_{\text{KCl}}$	<i>R</i>
KOn	3800	3510	1.086	1.042

TABLE XVII

SOLUBILITY OF NaON IN SODIUM NITRATE AND SODIUM CHLORIDE SOLUTIONS AT 0°

	0.1 <i>M</i> NaNO <sub>3</sub> × 10 <sup>3</sup>	0.1 <i>M</i> NaCl × 10 <sup>3</sup>	$P_{\text{NaNO}_3}/P_{\text{NaCl}}$	<i>R</i>
NaOn	9720	9280	1.051	1.025

*R* denotes, as explained the *n*th root of the ratio of solubility products, *n* being the number of ions of each salt. In order to calculate the ratios of interaction and the salting-out ratios from these data we use Equations 18 and 19 shown to be valid in the case of homo-ionic solvents also, *R*<sub>I</sub>, *R*<sub>II</sub> and *R*<sub>III</sub> corresponding to di-ionic, tri-ionic and tetra-ionic solutes, respectively.

A. Calculation of the Ratio of Interaction and the Salting-out Ratio for 0.1 *M* Potassium and Sodium Nitrate Solutions.—We have found (Table XIV) that *R*<sub>I</sub> = 1.025, *R*<sub>II</sub> = 1.030, and *R*<sub>III</sub> = 1.031.

Introducing these values into Equations 18 and 19,  $r_i = r_{\text{NO}_3(\text{Na/K})} = \left(\frac{R_{\text{II}}}{R_{\text{I}}}\right)^6 = \left(\frac{R_{\text{III}}}{R_{\text{I}}}\right)^4$  and  $r_u = r_{(\text{Na/K})} = \frac{R_{\text{I}}^4}{R_{\text{II}}^3} = \frac{R_{\text{I}}^3}{R_{\text{III}}^2}$  we obtain as the most fitting values  $r_i = 1.028$  and  $r_u = 1.011$ .

Again inserting these values into Equations 20, 21 and 22 we calculate the  $R$  values tabulated below together with the experimental values of  $R$ .

TABLE XVIII

COMPARISON OF  $R$  VALUES FOR POTASSIUM NITRATE AND SODIUM NITRATE SOLUTIONS

	$R_{\text{I}}$	$R_{\text{II}}$	$R_{\text{III}}$
Calc.	1.025	1.030	1.032
Found	1.025	1.030	1.031

showing that the adopted values of  $r_i$  and  $r_u$  agree excellently with the experiment.

**B. Calculation of the Ratio of Interaction and the Salting-out Ratio for 0.1 M Solutions of Potassium and Sodium Chlorides.**—The calculation is carried out quite similarly. Introducing the most fitting values:  $r_i = r_{\text{Cl}(\text{Na/K})} = 1.000$ ;  $r_u = r_{(\text{Na/K})} = 1.010$ ; we obtain the figures in Table XIX.

TABLE XIX

COMPARISON OF  $R$  VALUES FOR POTASSIUM AND SODIUM CHLORIDE SOLUTIONS

	Found	Calc.
$R_{\text{I}}$	1.010	1.010
$R_{\text{II}}$	1.009	1.010

The value for  $R_{\text{II}}$ , 1.009, is taken as the mean of the values 1.010 and 1.008 for  $[\text{Cl}]\text{Cl}_2$  and  $[\text{Br}]\text{Cl}_2$ , respectively. On account of the higher solubility of  $[\text{Cl}]\text{Cl}_2$ , the corresponding  $R_{\text{II}}$  value is certainly more accurate in these cases and using this value the agreement between  $R$  values found and calculated becomes complete.

**C. Significance of the Above Agreement.**—The above calculations led to two independent determinations of  $r_u = r_{(\text{Na/K})}$  at  $0^\circ$  namely:  $r_{(\text{Na/K})} = 1.011$ , and  $r_{(\text{Na/K})} = 1.010$ , using nitrates and chlorides respectively as solvents. In the previous section the same value 1.010 was found at  $20^\circ$  by means of tetranitro-diammine cobaltate dissolved in alkali nitrate solutions. We find thus through these measurements that the sodium ion has a salting-out effect about 1.0% larger than the potassium ion in 0.1 N solution. It is very desirable to test the scope of the present theory by further examinations in the same direction using as solvents various salt solutions with a common ion and salts of various types as solutes. It is interesting to note that the salting-out effects of 0.1 N solutions of potassium and sodium ions towards non-electrolytes differ in several cases by about the same amount. However, as

explained above, by using non-electrolytes as saturating substances we cannot assume the  $r_{(\text{Na}/\text{K})}$  to be precisely determined.

For the ratio of interaction we found  $r_{\text{NO}_3(\text{Na}/\text{K})} = 1.028$ , and  $r_{\text{Cl}(\text{Na}/\text{K})} = 1.000$ . While the chlorine ion is acted upon equally by potassium and sodium ions we see that the nitrate ion has an almost 3% higher avidity for the potassium ion than for the sodium ion.

The ratio of activity coefficients can now be calculated by means of Equation 19a

$$r_f = r_i r_u$$

yielding for the activity ratio of the nitrate ion

$$r_{\text{NO}_3(\text{NaNO}_3/\text{KNO}_3)} = 1.028 \times 1.011 = 1.039$$

while for the chlorine ion correspondingly:

$$r_{\text{Cl}(\text{NaCl}/\text{KCl})} = 1.000 \times 1.011 = 1.011.$$

The activity coefficient of the nitrate ion is thus about 4% higher in a 0.1 *N* solution of sodium nitrate than in a potassium nitrate solution of the same concentration, while in the case of the chlorides the corresponding value for the chlorine ion is about 1%.

## 8. Interrelation between Activity and Osmotic Coefficients and the Solubility and Freezing Point

Already in the first paper an interrelation between solubility and freezing point was suspected, because a solvent having a small freezing-point lowering generally proved of high dissolving power towards a slightly soluble salt and *vice versa*. A simple relation, however, could not be found, because the ratio of dissolving power of two solvents varies with the nature of the saturating salt. This problem is readily solved by introducing the principle of the specific interaction of ions in connection with a general thermodynamic treatment of the relation between activity and osmotic coefficients in a mixed solution of constant total concentration.

The general relation<sup>14</sup>

$$\sum c_i d \ln \xi_i = d\eta \quad (27)$$

where  $c_1$  and  $\xi_1$  stand for the concentration and the activity of the first ion,  $\eta$  for the osmotic concentration and  $\sum c_i = c$  is the total ion concentration, forms a basis for such treatment.

Introducing in this equation  $\xi_i = c_i f_i$  and  $\eta = c\phi$  and assuming  $c$  to be constant we obtain

$$\sum c_i d \ln c_i + \sum c_i d \ln f_i = c d\phi \quad (28)$$

or

$$\sum c_i d \ln f_i = c d\phi \quad (29)$$

<sup>14</sup> Ref. 8, p. 761.

If we now consider a mixed solution of potassium and sodium chlorides

in which  $\frac{c_{\text{NaCl}}}{c_{\text{KCl}}} = \frac{x}{1-x}$  we can write

$$c_{\text{NaCl}} = \frac{c}{2}x; \quad c_{\text{KCl}} = \frac{c}{2}(1-x); \quad c_{\text{Cl}} = \frac{c}{2}$$

and thus

$$x \, d \ln f_{\text{Na}} + (1-x) \, d \ln f_{\text{K}} + d \ln f_{\text{Cl}} = 2d\phi \quad (30)$$

by which the activity coefficients of the ions in the mixed solution are thermodynamically correlated to the osmotic coefficients.

We shall now introduce the principle of the specific interaction of ions. Since, according to this, the coefficients of interaction of the cations are unchanged when the solution gradually changes from a potassium to a sodium chloride solution because the only interacting ion,  $\text{Cl}^-$ , is present in constant concentration, the change in  $f_{\text{K}}$  and  $f_{\text{Na}}$  is due to the changing salting-out effect alone. We, therefore, can put

$$d \ln f_{\text{K}} = d \ln f_{\text{Na}} = d \ln f_u \quad (31)$$

and

$$d \ln f_u + d \ln f_{\text{Cl}} = 2d\phi; \quad (32)$$

or in integrated form

$$\phi_{\text{NaCl}} - \phi_{\text{KCl}} = \frac{1}{2} \ln \frac{f_{(\text{Na})}}{f_{(\text{K})}} + \frac{1}{2} \ln \frac{f_{\text{Cl}(\text{NaCl})}}{f_{\text{Cl}(\text{KCl})}}, \quad (33)$$

or by means of (5)

$$\phi_{\text{NaCl}} - \phi_{\text{KCl}} = \frac{1}{2} \ln \frac{f_{\text{Cl}(\text{Na})}}{f_{\text{Cl}(\text{K})}} + \ln \frac{f_{(\text{Na})}}{f_{(\text{K})}} \quad (34)$$

These equations can also be written

$$\phi_{\text{NaCl}} - \phi_{\text{KCl}} = \ln [r^{1/2}_{\text{Cl}(\text{Na/K})} r_{(\text{Na/K})}] = \frac{1}{2} \ln [r_{\text{Cl}(\text{NaCl/KCl})} r_{\text{Na/K}}] \quad (35)$$

In the more general case of the two salts aluminum sulfate and ferric sulfate we obtain by quite similar calculations,

$$2 \, d \ln f_u + 3 \, d \ln f_{\text{SO}_4} = 5d\phi \quad (36)$$

or

$$\phi_{\text{Al}_2(\text{SO}_4)_3} - \phi_{\text{Fe}_2(\text{SO}_4)_3} = \frac{2}{3} \ln \frac{f_{\text{SO}_4(\text{Al}_2(\text{SO}_4)_3)}}{f_{\text{SO}_4(\text{Fe}_2(\text{SO}_4)_3)}} + \frac{2}{3} \ln \frac{f_{(\text{Al})}}{f_{(\text{Fe})}} \quad (37)$$

and

$$\phi_{\text{Al}_2(\text{SO}_4)_3} - \phi_{\text{Fe}_2(\text{SO}_4)_3} = \frac{2}{3} \ln \frac{f_{\text{SO}_4(\text{Al})}}{f_{\text{SO}_4(\text{Fe})}} + \ln \frac{f_{(\text{Al})}}{f_{(\text{Fe})}} \quad (38)$$

yielding, for instance, for magnesium and calcium chlorides

$$\phi_{\text{MgCl}_2} - \phi_{\text{CaCl}_2} = \frac{2}{3} \ln \frac{f_{\text{Cl}(\text{MgCl}_2)}}{f_{\text{Cl}(\text{CaCl}_2)}} + \frac{1}{3} \ln \frac{f_{(\text{Mg})}}{f_{(\text{Ca})}} = \frac{2}{3} \ln \frac{f_{\text{Cl}(\text{Mg})}}{f_{\text{Cl}(\text{Ca})}} + \ln \frac{f_{(\text{Mg})}}{f_{(\text{Ca})}} \quad (39)$$



and for potassium and sodium sulfates

$$\varphi_{\text{Na}_2\text{SO}_4} - \varphi_{\text{K}_2\text{SO}_4} = \frac{1}{2} \ln \frac{f_{\text{SO}_4(\text{Na}_2\text{SO}_4)}}{f_{\text{SO}_4(\text{K}_2\text{SO}_4)}} + \frac{1}{2} \ln \frac{f_{(\text{Na})}}{f_{(\text{K})}} = \frac{1}{2} \ln \frac{f_{\text{SO}_4(\text{Na})}}{f_{\text{SO}_4(\text{K})}} + \ln \frac{f_{(\text{Na})}}{f_{(\text{K})}} \quad (40)$$

A relation between solubility and osmotic coefficients of the solvents is now easily arrived at by writing Equation 22 as follows.

$$\frac{1}{2} \ln \frac{P_{\text{AgCl}(\text{KCl})}}{P_{\text{AgCl}(\text{NaCl})}} = \frac{1}{2} \ln \frac{f_{\text{Cl}(\text{Na})}}{f_{\text{Cl}(\text{K})}} + \ln \frac{f_{(\text{Na})}}{f_{(\text{K})}} \quad (41)$$

which by comparison with (34) gives

$$\varphi_{\text{NaCl}} - \varphi_{\text{KCl}} = \frac{1}{2} \ln \frac{P_{\text{AgCl}(\text{KCl})}}{P_{\text{AgCl}(\text{NaCl})}} \quad (42)$$

The corresponding relations for the more general case of  $\text{L}_2(\text{SO}_4)_3$  dissolved in aluminum sulfate and ferric sulfate solutions give

$$\varphi_{\text{Al}_2(\text{SO}_4)_3} - \varphi_{\text{Fe}_2(\text{SO}_4)_3} = \frac{1}{2} \ln \frac{P_{\text{L}_2(\text{SO}_4)_3(\text{Fe}_2(\text{SO}_4)_3)}}{P_{\text{L}_2(\text{SO}_4)_3(\text{Al}_2(\text{SO}_4)_3)}} \quad (43)$$

The difference in osmotic coefficients, and therefore in freezing points, of two solutions with a common ion, may thus be computed from the solubility ratio of a sparingly soluble salt possessing also the common ion of the solvents; and *vice versa*, solubility ratios can be calculated from freezing-point measurements.

In a quite similar way solubility measurements in hetero-ionic solvents may be utilized for the same purpose. According to Equations 8 and 14

$$\ln \frac{S_{\text{AgCl}(\text{KNO}_3)}}{S_{\text{AgCl}(\text{NaNO}_3)}} = \frac{1}{2} \ln \frac{f_{\text{Cl}(\text{Na})}}{f_{\text{Cl}(\text{K})}} + \ln \frac{f_{(\text{Na})}}{f_{(\text{K})}} \quad (44)$$

and

$$\ln \frac{S_{\text{L}_2(\text{CrO}_4)_3(\text{Fe}_2(\text{SO}_4)_3)}}{S_{\text{L}_2(\text{CrO}_4)_3(\text{Al}_2(\text{SO}_4)_3)}} = \frac{1}{2} \ln \frac{f_{\text{CrO}_4(\text{Al})}}{f_{\text{CrO}_4(\text{Fe})}} + \ln \frac{f_{(\text{Al})}}{f_{(\text{Fe})}} \quad (45)$$

and thus

$$\ln \frac{S_{\text{AgCl}(\text{KNO}_3)}}{S_{\text{AgCl}(\text{NaNO}_3)}} = \varphi_{\text{NaCl}} - \varphi_{\text{KCl}} \quad (46)$$

and

$$\ln \frac{S_{\text{L}_2(\text{CrO}_4)_3(\text{Fe}_2(\text{SO}_4)_3)}}{S_{\text{L}_2(\text{CrO}_4)_3(\text{Al}_2(\text{SO}_4)_3)}} = \varphi_{\text{Al}_2(\text{CrO}_4)_3} - \varphi_{\text{Fe}_2(\text{CrO}_4)_3} \quad (47)$$

Equation 42 can be tested by means of the solubility data from Tables XIV to XVII and available data of the freezing-point lowerings of alkali nitrates and chlorides taken from the critical study of Noyes and Falk. The figures are collected in Table XX.

TABLE XX  
COMPARISON OF FREEZING-POINT AND SOLUBILITY DATA

Salt <sub>1</sub>	Salt <sub>2</sub>	$\Delta t_1 - \Delta t_2$	$\varphi_1 - \varphi_2$	$P_2/P_1$	$1/2 \ln(P_2/P_1)$
$\text{NaNO}_3$	$\text{KNO}_3$	0.090	0.024	1.051	0.025
$\text{NaCl}$	$\text{KCl}$	0.027	0.008	1.020	0.010
$\text{KCl}$	$\text{KNO}_3$	0.148	0.039	1.086	0.041
$\text{NaCl}$	$\text{NaNO}_3$	0.085	0.023	1.051	0.025

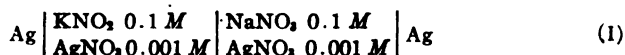
According to Equation 42 we have  $\varphi_1 - \varphi_2 = \frac{1}{2} \ln (P_2/P_1)$ .

The figures in the second and fourth columns show this relation to be fulfilled very exactly and thus lend strong support to the theory on which these calculations are based.

### 9. Determination of the Liquid-junction Potential on the Basis of our Principles

The principles established in the preceding sections can clearly be utilized for estimating the liquid junction potential in a galvanic cell.

If we wish to determine the potential  $\pi_d$  at the liquid junction,  $0.1 M \text{ KNO}_3 \mid 0.1 M \text{ NaNO}_3$ , we add a little silver nitrate and measure the cell



the electromotive force of which is given by the equation

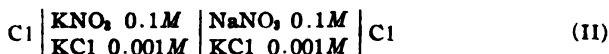
$$\pi_1 = RT \ln \frac{f_{\text{Ag}(\text{NaNO}_3)}}{f_{\text{Ag}(\text{KNO}_3)}} + \pi_d \quad (48)$$

or according to our principles

$$\pi_1 = RT \ln r_{(\text{Na}/\text{K})} + \pi_d \quad (49)$$

Since  $r_{(\text{Na}/\text{K})}$ , as shown, may be determined from solubility measurements we are in a position to calculate  $\pi_d$  from the electromotive force of the cell found.

Adding a little chloride to the two nitrate solutions we can build the following cell



yielding the electromotive force

$$\pi_2 = RT \ln \frac{f_{\text{Cl}(\text{KNO}_3)}}{f_{\text{Cl}(\text{NaNO}_3)}} + \pi_d$$

or

$$\pi_2 = -RT \ln [r_{(\text{Na}/\text{K})} r_{\text{Cl}(\text{Na}/\text{K})}] + \pi_d \quad (50)$$

equally usable for estimation of  $\pi_d$ .

Combining Equations 49 and 50 we obtain

$$\frac{\pi_1 - \pi_2}{2} = RT \ln [r^{1/2}_{\text{Cl}(\text{Na}/\text{K})} r_{(\text{Na}/\text{K})}] \quad (51)$$

or by introduction of (II)

$$\frac{\pi_1 - \pi_2}{2} = RT \ln \frac{S_{\text{AgCl}(\text{KNO}_3)}}{S_{\text{AgCl}(\text{NaNO}_3)}} \quad (52)$$

showing an important relation to hold between solubility and electromotive force.

It is obvious that when  $r_{\pm}$  has been determined from solubility measurements and therefore  $\pi_d$  can be computed by means of Equation 49 from measurements of the cell (I) then Equation 49 can be generally utilized for the determination of  $r_{\pm}$ , the ratios of interaction, inserting in the solutions various electrodes and adding small amounts of the corresponding salts.

Since for  $r_{(\text{Na}/\text{K})}$  the value 1.010 has been found above, the liquid junction potential in a cell like (I) containing potassium and sodium associated with the same anion is given by  $\pi_d = \pi_1 - 0.00025$  volt at  $20^\circ$ . The two  $\pi$ 's are here reckoned in the direction from  $\text{K}^+$  to  $\text{Na}^+$  solution.

### Summary

1. The activity coefficient of an ion may be determined by two factors, one of which is due to the salting-out effect of the salt solution serving as solvent and the other to electrical interaction between the said ion and the ions of the solvent.
2. Ions are uniformly influenced by ions of their own sign. Their activity coefficients depend, therefore, only upon the action of ions of opposite sign and the salting-out effect of the solvent.
3. The salting-out effect of a salt solution can be represented as a product of the salting-out effects of the separate ions.
4. Simple relations regarding solubility in salt solutions at constant concentration are derived.
5. Methods for determining the ratios of salting-out coefficients, coefficients of interaction and activity coefficients are given.
6. A thermodynamic relation between activity coefficients and osmotic coefficients in solutions of constant total concentration, and a relation between solubility and freezing point are derived.
7. A method for estimating liquid-junction potentials is found.
8. The theoretical conclusions in the paper are experimentally verified.

COPENHAGEN, DENMARK

## THE MAINTENANCE OF THE ADIABATIC CONDITION IN CALORIMETRY

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In recent communications to *THIS JOURNAL*<sup>1</sup> a procedure was described by which the heats of slow reactions lasting 6 hours or more could be measured with precision. By an illustrative determination, the heat of inversion of sucrose by acid was fixed within an extreme experimental discrepancy of 4 gram-calories, which represented a variable error but little greater than that observed in the similar measurement of reactions complete in 10 minutes. This indicated that the precision of the protracted measurements was limited more by defects inherent in the general method than by imperfect control of the minute but slowly cumulative leakage which the procedure had been designed to minimize. There was, on the other hand, no evidence to show that such leakage had been prevented; indeed systematic errors were suspected, and the accuracy of the determinations was acknowledged to be in doubt. The present paper describes an attempt to discover the sources of both the variable and the constant errors which significantly affect measurements of this type, and thus to establish for them a workable standard of true accuracy. The attempt has been successful to this extent: that all thermal disturbances appear to be identified, which in protracted determinations 10 hours long are likely to cause errors of half a gram-calorie or more. The possibility of eliminating these effects (by means which the present work suggests) is now being tested by a more minute examination of the sucrose inversion. Meanwhile the results here presented possess a certain interest in themselves, since in many ways they are of general applicability.

### Thermal Disturbances Examined

In nearly all precise adiabatic calorimetry heretofore, an open calorimeter has been used, surrounded, at least laterally and below, by very narrow air spaces, and stirred reciprocally.<sup>2</sup> The thermal disturbances recognized as sources of probable error in the preceding research were for the most part characteristic of this type of system. They had been traced to the following sources: (1) direct conduction leakage between calorimeter and outer environment through thermometer, stirrer rods and operating mechanism, and through the insulations which enclosed these parts; (2) direct convection leakage between calorimeter and outer environment, caused by the pumping of air by reciprocating stirrers; (3) complicated disturbances of leakage between calorimeter and bath, caused by the accidental presence of moisture in the insulating air gaps, and

<sup>1</sup> *THIS JOURNAL*, 42, 1295, 1911 (1920).

<sup>2</sup> See *ibid.*, 37, 994 (references) and 1006 (1915); *ibid.*, 38, 1475 (1916); 39, 2113 (1917); 42, 1623 and 1914 (1920). But cf. *Bur. Standards Bull.*, 11, 210ff.

by various superimposed effects of evaporation from the open system; (4) imperfectly adiabatic initial conditions due to similar causes, themselves the result of diverse prior conditions; (5) various effects of transmission and distribution lags; (6) possible irregularities in the production of stirring heat; (7) thermometric uncertainties caused by environmental influences.

The present investigation comprised an examination of all these sources of uncertainty.

### Thermometry

Temperatures were determined by the twin mercury thermometers previously used and elsewhere described.<sup>3</sup> The reading error of these instruments was less than  $0.0005^{\circ}$ . The probable error of calibration, never greater than  $0.0010^{\circ}$ , was for the small temperature differences observed, which were read on selected ranges, considerably less than this.<sup>4</sup> There was no evidence of significant capillary friction with changes more rapid than  $0.002^{\circ}$  per hour, and the few irregular fluctuations of this magnitude which were observed were of ambiguous origin.<sup>5</sup> In all cases where such irregularity was apt to cause significant error, the measurement was checked by change of procedure. The thermometers were installed and manipulated as formerly, so as to eliminate the danger of irregular registrations due to dissimilar or variable immersions and exposures; and were further protected from the body heat of the operator by a mirror, and from the possible effects of illumination by water screens, which adequate tests showed to be completely effective. Thermometric lag introduced no errors. In every measurement the total thermometric error, thus made determinable and always estimated, was found to be too small to invalidate inferences drawn from the relations of the thermal effects measured,<sup>6</sup>

<sup>3</sup> Ref. 1, pp. 1918-1920.

<sup>4</sup> The calibration had been made by comparison with normal instruments (made by Baudin and standardized by the Bureau des Poids et Mesures) in a carefully controlled adiabatic system. Sixteen points in three groups, each of which covered the total range of  $0.6^{\circ}$ , were thus determined, and checked each other with remarkable nicety. In measurements of small changes of temperature, the ranges selected were on smooth slopes of the calibration curves close to chosen determined points. Larger temperature changes were measured over the complete segments between determined points. In this manner errors of interpolation were largely avoided.

<sup>5</sup> That is, possibly due to thermal inhomogeneity within the calorimeter, to abrupt irregularity of capillary bore, or to momentary change of stem temperature.

<sup>6</sup> In the measurements of the heats of stirring at lowest speeds (Tables I and II), of leakage rates due to conduction between calorimeter and outer environment (Table IV), of the final and vanishing rates of temperature change caused by surface adsorption of moisture (Table IX), and of certain thermal leakages between calorimeter and bath under heads of  $0.1^{\circ}$  (Table V), the total temperature changes observed were less than  $0.01^{\circ}$ . In these cases, thermometric error caused uncertainties of measurement amounting to 10% or more. But all these data were either checked by repetition or were confirmed by their concordance with the results of more dependable measurement. In the succeeding tables, the error of observation for every recorded rate of temperature

and the continued use of these instruments was thus for the time being justified.<sup>7</sup>

### Control of Outer Environmental Temperature

The constant temperature closet previously built<sup>8</sup> and later considerably improved was used throughout. Since a very carefully controlled environmental temperature appears to be essential in protracted calorimetry (p. 916 and Table IV), this device merits a brief description. The closet was built of wood with double walls and floor in the middle of a cellar laboratory. Its walls were pierced near the ceiling with adjustable apertures, so that when the temperature outside it remained 2° or more below that within, the latter could be made naturally to fall at a rate fairly definite and not too slow. By means of ice water flowing through a grid on the ceiling, this natural fall could be maintained also within the closet itself, so that it could be used in hot as well as in cold weather. Against this temperature fall an electrical heating and distributing mechanism operated, so as to establish a slightly fluctuating temperature. The control was maintained by a bimetallic regulator and relay arrangement, in all essentials similar to those commonly used with water thermostats. In principle, therefore, the room was a thermostat of this type.

To make a fairly uniform distribution possible, the heating device was built on the outer wall of the closet. A small blower fan sucked air slowly upward through a vertical insulated box containing adjustable resistances, change may be computed by comparing the temperature changes observed (rates  $\times$  durations) with 0.0010° (maximal thermometric error) or with 0.0005° (the probable thermometric error).

<sup>7</sup> The data provided by this investigation give support to the opinion that excepting in rare instances, the calorimetric uncertainty—that due to the effects of natural thermal disturbances in imperfectly controlled systems—has been in the past considerably greater than the necessary thermometric error of mercury instruments. Such usually (cf. p. 934) has been the case whenever open calorimeters have been used, or whenever in determinations carried out with closed systems no particular precautions have been taken to avoid surface contaminations or the presence of water in the air gap. It is always likely to be the case whenever undetermined lags occur, and is inevitably so in all protracted determinations. If, in addition, the errors which are characteristic of particular physico-chemical processes are considered, it will be apparent that the use of mercury instruments will continue to be advantageous in all experimental work designed to establish the efficacy of special calorimetric procedures. When, however, these sources of uncertainty have been brought under definite control, a more exact electrical thermometry will certainly justify itself. The most troublesome defects of mercury thermometers, particularly those due to large and uncertain errors of calibration, to the necessity of stem exposure, and to capillary friction, may doubtless be considerably improved; and the possibility of such improvement merits consideration. There is no doubt, however, that the technique of the most precise mercury thermometry is already about as exacting as any other.

<sup>8</sup> Ref. 1, p. 1915.

where it was heated to any desired temperature. In hot weather a grid of metal plates, through which ice water flowed continuously, replaced the coils. From this box the air was blown across the regulated heating lamps, which were held in a horizontal metal box of somewhat smaller cross section, uninsulated and set out from the wall (so that it radiated freely and was without great lag) and was delivered into the closet through a hopper shaped frame so placed that the incoming stream, if unchecked, would not impinge upon any operating mechanism. It was then caught between two horizontal and opposed air currents from swinging eight-inch fans, and was thus scattered. Smoke tests showed that the distribution thus effected was sufficiently rapid. The ventilation was, of course, excellent. The space ( $4.0 \times 2.7 \times 2.7$  meters) was sufficient for two calorimeters with all desirable accessories, and could be used by two operators without disagreeable crowding.<sup>9</sup>

The closet held necessary water in a single closed 150-liter tank, fed from a similar tank above it on the outer side of the wall. In this tank water was heated uniformly and automatically to calorimeter temperature before it was introduced. Residual water in the inner tank was similarly brought to the same temperature before measurements were made.<sup>10</sup>

The illumination of the closet was direct, from water-screened tungsten filament lamps, and the walls and large fixtures were painted black. This defined the sources of possible irregularities from radiation effects in all measurements. It is, however, probable that brighter indirect illumination in a white walled room would have been safe enough.

By these arrangements the temperature in the vicinity of the calorimeter was continuously held to within  $0.2^\circ$  or even  $0.1^\circ$  of the calorimetric. As will be shown later, this control was necessary but sufficient to reduce the correction for direct leakage between the calorimeter and its outer environment during 10 hours or less to magnitudes calculable without significant error from the determined leakage rates for large thermal heads (Table IV).

### New Modifications of Calorimeters

The calorimeters used were two similar systems of the approximate dimensions and heat capacities most practical for general thermochemical work.<sup>11</sup> They were built to accommodate without essential modification

<sup>9</sup> A closet formerly used ( $3.6 \times 1.8 \times 2.4$  meters) was not only inconvenient even for one operator, but was less easily regulated. In this construction, the air was taken from the closet itself instead of from the outside laboratory. Such construction eliminates the preheating and precooling boxes, but necessitates the installation of a ventilating fan. It is less flexible than the present arrangement, but would serve well in case gases were set free within the room.

<sup>10</sup> It is unnecessary to make a thermostat out of the inner tank.

<sup>11</sup> For the sake of possible future comparisons of data, the essential figures are here given: height of open cylindrical vessel, 152 mm., of closed vessel, 154 mm.; diameter,

any type of thermometric instrument, various inner vessels, electrical resistance, accessory thermo-elements and so on, and they were provided with several jackets by which they could be surrounded by air spaces of various widths and configurations, and with external mechanisms by convenient adjustment of which they could be stirred reciprocally at several speeds by one or two stirrers operating in conjunction or opposition, continuously or intermittently. A single cylindrical calorimetric vessel of gold-plated

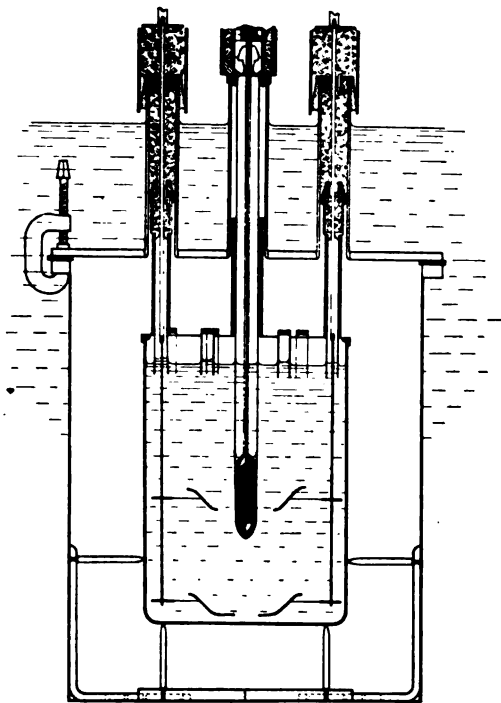


Fig. 1.—Closed calorimeter with 40mm. jacket. Metal is blank, or, as wire or sheet, is black; vulcanite is heavily and rubber lightly hatched; wax or kneaded rubber, cross hatched. Mercury, mirror surfaces and cement are black; ivory and glass are unmarked.

Parts behind the (diametrical) section are lightly drawn. The calorimeter support is represented as having 4 arms; in reality it has 3. The stoppered apertures in the calorimeter cover are those for a second stirrer and electrical leads. They help to indicate the whole extent of metallic connection between calorimetric liquid and cover. Other accessory contrivances not used in this work are not drawn. Reduced to one-quarter actual size.

108 mm.; heat capacity here invariably used, 1234 gram-calorie units for both closed and open systems.



copper was used throughout. This was fitted with a brass cover which bore vertical chimneys of vulcanite to accommodate thermometer and stirrer rods, and which, excepting at the stirrer apertures, could be made vapor-tight by gaskets of kneaded rubber. The cover was in thermal contact with the calorimeter water through inner brass extensions of the chimney collars as well as through the vessel walls. It was thus held closely enough at calorimeter temperature during the slow changes here measured.<sup>12</sup> The calorimeter thus arranged is that designated in the sequel "the closed calorimeter." Without the cover it is called "the open calorimeter." In all other respects excepting for their insulations, the two systems were alike. In the determinations the vessels were filled with such definite weights of water that their total heat capacities were the same and invariable within the percentage error of measurement, and the same thermometer and stirrer were used with both.

The jackets were of the general type heretofore employed. Four of these jackets were used in this work, of such internal dimensions that when they held the closed calorimeter, the air gaps which surrounded it were uniformly 10, 20, 30, and 40 mm. wide. The jacket rims were all made of the same external diameter, so as to fit a single cover, a plate of rolled brass into which chimneys corresponding to those on the calorimeter cover but larger, were tapped and soldered. Closure was effected against

<sup>12</sup> For sealing the calorimeter, kneaded rubber was found preferable to wax, which by smearing was likely to affect the surface of the calorimeter and to contaminate its contents. The rim gasket here used, placed at the inner edge of the cover, suffices for measurements with water, but in chemical operations it should be placed outside as, for instance, between the edge of the cover rim and a ring firmly attached to the outer vessel wall a little below the top. A construction possibly safer in the measurement of more rapid changes would be that described by White [*Phys. Rev.*, 25, 137 (1907); 31, 574, 671 (1910)]; a depression of the central cover surface which touches the surface of the contained liquid. This device, however, would restrict unfavorably the working space within the calorimeter. The use of oil seals with such construction would, of course, be inadvisable in chemical operations, and would justify itself in any case only if evaporation, the rate of which would be modified in an unpredictable way by slight surface contamination with oil, were wholly prevented. In adiabatic work, particularly in the measurement of slow processes, a space between the calorimeter liquid and a close fitting and highly conducting cover is not a disadvantage whenever the adiabatic condition can be closely maintained. Distillation between cover and liquid, slight even under very imperfect adiabatic conditions, amounts to nothing more than added internal distribution lag.

The vulcanite chimneys seem at first sight a more serious defect in construction. It is almost certain, however, that in adiabatic work, when the temperature of the bath fluctuates slightly about that of the calorimeter, they will have no appreciable lag, since their own heat capacity is a very small fraction of the whole, and since under these conditions they will transmit no measurable heat to and from the system. In many of the present measurements, in which fairly large thermal heads were established between calorimeter and bath, the chimneys must have introduced a considerable lag; the effect of this and of other lags was, however, eliminated by establishing in every measurement a uniform rate of flow under constant head, before readings were accepted for record.

soft rubber gaskets by loose clamps, conveniently manipulated with a socket wrench. Within the jackets the calorimeter rested upon and was centered by pointed ivory rods, cut to the exact widths of the several desired gaps and screwed into sockets on a radically adjustable and rigid frame. This was secured in the looser jackets by graduated wedges with which it could be symmetrically adjusted. The dimensions of the jackets were, however, sufficiently uniform and exact to make the actual widths of the air gaps so close to multiples of 10 mm. that they could be accepted as such without significant error. The jackets and jacket cover were nickel plated and highly polished inside, and the outer surfaces of the calorimeter were similarly, though not so perfectly, reflecting.

To prevent significant leakage through the stirrer apertures of the closed calorimeter, the following construction was adopted. The stirrer wires at a point which lay 10 mm. above the liquid surface when the stirrer was in its lowest position, were tapped

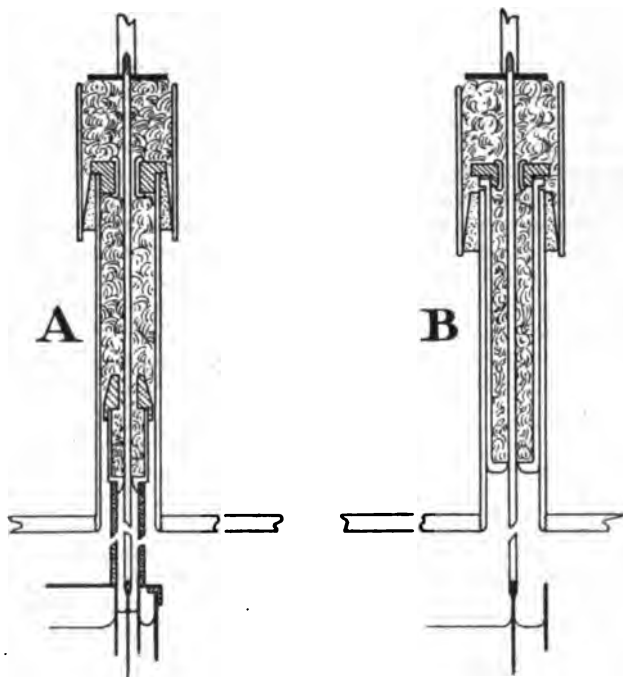


Fig. 2.—Detail of stirrer insulations: A, for closed calorimeter; B, of open calorimeter. One-half actual size.

into polished rods of ivory less than 2 mm. in diameter. Within the vessel these rods were wholly enclosed by those inner extensions of the narrow brass collars of the chimneys through which intimate thermal contact between cover and calorimeter liquid had been effected. Thence they extended through the vulcanite chimneys. These were of such length that they traversed the widest upper basal gap and entered the corresponding chimneys of the jacket cover. They were surmounted by cylindrical brass boxes, pierced below with conical apertures just large enough to receive the rods, and filled with cotton wool firmly compressed and held in position by threaded vulcanite caps. This arrangement reduced the total volume of water-saturated air set in motion by the stirrers, and thus minimized convection in the chimneys, permitted no conduction of

heat through stirrer wires into the insulation, and ensured a dry and compressed packing which held practically still air. All frictional heat due to scraping was developed in the boxes and was conducted through the brass into a narrow ring of air in close contact with the bath, so that it affected neither the calorimeter nor the insulating spaces. The narrow aperture of the box served also to steady the motion of the stirrer. Above the vulcanite chimneys, the jacket chimneys into which they extended were also stopped with cotton wool, held in place by perforated rubber stoppers lined with glass; and at the top were fitted with glass tubes similarly filled, which served primarily to prevent any contamination of the insulation beneath by spattering from the bath.<sup>13</sup>

The apparent efficacy of this form of closure for the covered calorimeter suggested the advisability of closing the air gap in a similar way when the open calorimeter was used. The usual stirrer chimney insulation heretofore employed—cotton wool held loosely or enclosed in glass tubes at the chimney tops—is very slightly effective on account of the large surfaces exposed to environmental temperatures, as will be shown in any case by rough calculations from the dimensions and thermal conductivities. In these measurements, therefore, the insulation was held in heavy brass cartridges, pierced with small apertures below, and closed above with perforated rubber stoppers lined with glass, which fitted snugly into the jacket stirrer chimneys throughout their entire length. By this device the stirrer rods from the open calorimeter were made to pass through long tubes of cotton wool insulation, the lateral areas of which were kept at bath temperature, so that conduction leakage through them was very small indeed. The efficacy of these insulations was demonstrated by the constancy with which the isothermal condition could be maintained (p. 908); by the very slightly variable heating caused by fast continuous stirring of uniform speed in different assemblages (p. 909); by the small leakages between calorimeter and outer environment which resulted from conduction and convection through the stirrer orifices (Table IV and Ref. 28); and by the results of certain measurements (Table III) in which while slow continuous stirring was maintained, the leakage rates were identical under positive and negative bath heads as great as  $1^{\circ}$ .

In both constructions, the ivory rods extended into the outer air, where they were screwed into metal rods, which in turn were attached by nuts securely but loosely to the stirrer hanger. The operating mechanism was that employed before, modified by the inclusion of an extra countershaft and pulleys which permitted its adjustment to several speeds. The variability of these speeds was slight, and introduced after suitable correction according to former practice<sup>14</sup> no appreciable irregularities into the calculation of stirring heats. The stirrer itself was a perforated 2-stage ring provided with extra blades so disposed that with every stroke the calorimeter liquid was very thoroughly agitated. The thermal effects of stirring are discussed further on (p. 909).

The bath was regulated by ice water and sulfuric acid drips as heretofore so that its temperature fluctuated about that of the calorimeter over a range of less than  $\pm 0.01^{\circ}$ . Correction was always made for leakage between calorimeter and bath on the assumption

<sup>13</sup> Other forms of closure were, of course, possible. The simple device of flexible rubber tubes attached to stirrer rods and chimney tops and certain practicable though more or less elaborate forms of liquid seal closures were, despite their probably greater efficiency, left untried because of the eddying air currents they were likely to set up in the air gaps.

In one test of the adiabatic insulation, the cotton wool in the boxes was saturated over its middle zone with heavy cylinder oil. The precaution was quite practicable, for no oil leaked out; but it proved to be unnecessary. Vaseline was too viscous to be used advantageously in this way.

<sup>14</sup> From the data of Table I and according to the procedure of Ref. 1, p. 1936.

previously made that the leakage was proportional to thermal head. The leakage measurements hereafter described (pp. 918, 934; Tables V and X) proved that this assumption alone involved no significant error in measurements made either with the closed or with the open system. The bath was stirred by 2 multiple paddles, so effectively that having been locally warmed or cooled by the drips, it always came to complete thermal homogeneity within 50 seconds. This delay was the same for rise and fall of temperature, and introduced compensating errors into the record of its slight and regular fluctuation which calculations from the minute data of former protracted measurements proved to be quite negligible. It was probable that the thermal inhomogeneity of the bath was too small to affect sensibly the uniform distribution of heat over the highly conducting jackets: these, therefore, were assumed to be at every instant during measurement practically isothermal.<sup>15</sup> Convection lag within the jackets was certainly quite negligible.<sup>16</sup> The volume of the largest air gap was 4.8 liters. Its heat capacity at the temperature of measurement, 1.4 gram-calorie units, was too small to affect the results of usual measurement even if it were wholly neglected (Ref. 11) and in any case its effective heat capacity could be estimated with negligible error. Calculation from its determined thermal conductance (Table VIII) also showed that under the adopted bath control its conduction lag would be too small to affect with significant error the calculation of the thermal transfer between calorimeter and bath, which ignored this effect.<sup>17</sup> It is therefore apparent that neither the heat capacity nor the total thermal lag of the widest air gap could have any perceptible effect on the results of protracted measurements made with systems similar to those here employed; and that, finally, the procedure formerly adopted for the reduction and correction for leakage between calorimeter and bath involved no significant error. This correction was never greater than  $0.0005^{\circ}$ ; and when the wider gaps were used, was wholly negligible.

<sup>15</sup> The convection leakages under very small heads suggested, however, that they may not have been so (Ref. 37).

<sup>16</sup> There was no need to attempt the difficult determination of such lag. Under an adiabatic control even carelessly maintained, the temperature difference between calorimeter and bath will never be greater than  $0.1^{\circ}$ . With a 10- or a 20mm. air gap, the total convection leakage under this head is not more than 0.013 g.-cal. per minute, and with the 40mm. gap it is about half as much (Table VI and Ref. 11). Even if this leakage were wholly prevented by lag, the resulting effect during periods of mixture, which when properly conducted are not longer than 5 minutes, and upon correspondingly large bath fluctuations of similar duration due to accident, would be negligible. The analogous effect on the leakage into a bath held continuously at a mean temperature  $0.01^{\circ}$  lower than the calorimeter would be, if the narrowest (10 mm.) gap were used, less than 0.0013 g.-cal. per minute, or 0.8 cal. in 10 hours, but in practice the bath fluctuates about the calorimeter temperature within a range of less than  $\pm 0.01^{\circ}$  and the effect is, again, negligible.

<sup>17</sup> The maximum bath head was  $0.01^{\circ}$ ; the mean head of the insulating air, therefore, averaged  $0.005^{\circ}$ , and its average excess or deficiency of heat while leakage was constant under the maximal bath head was  $1.4 \times 0.005 = 0.007$  cal. Since the thermal conductance under  $0.01^{\circ}$  head was 0.010 cal. per minute (Table VIII and Ref. 11) this heat at the maximum head would be delivered in  $0.007 \div 0.010 = 0.7$  minute. It would therefore be in considerable part delivered during the reversal of the bath. Assuming such reversals to occur not oftener than every 10 minutes (the usual practice) or 60 times in 10 hours, the total heat retained by the gap from leakage in one direction would average less than  $60 \times 0.007 = 0.4$  cal.—a quantity itself negligible, amounting to no more than  $1/3$  of this leakage, and largely, if not wholly, compensated by the similar effect on leakage in the opposite direction.

### Establishment of the Isothermal Condition

When the closed calorimeter equipped with thermometer and stirrer was held in a dry air<sup>18</sup> space with the bath kept fluctuating within  $\pm 0.01^\circ$  and the outer environment within  $\pm 0.2^\circ$  of the temperature within, it could be and was repeatedly maintained isothermal for 3 hours or more within the range of thermometric sensitivity. The duration of these tests and their variety with respect to absolute temperature and prior condition made it very improbable that this apparent constancy was due to anything but a real equilibrium.<sup>19</sup>

With the closed calorimeter in a dry gap, this condition was always easily established. With the open calorimeter, on the contrary, great difficulty was encountered, due not only to evaporation leakages, which could be prevented by saturating the gap with water, but to various protracted thermal disturbances caused by the surface adsorption of moisture and the occasional isothermal distillation from droplets which accompanied readjustments from diverse prior conditions (p. 934. Cf. p. 931). These effects could be most certainly eliminated by enclosing the open vessel in a dry gap and allowing it to rest at constant temperature for several hours (conveniently overnight) until equilibrium was established, a procedure which necessitated a thermostatic regulation of the bath. Such regulation could be avoided only by bringing the bath before measurement to the desired temperature, and holding it there while the jacket surfaces and that of the calorimeter, previously heated to a temperature somewhat higher, were slightly wetted and allowed to dry until the adhering water was almost invisible. Then, after quick assemblage, it was not impossible that equilibrium could be established within an hour, but this was by no means certain. In the long run, time would be saved by the former procedure.<sup>20</sup> In either way, however, an isothermal condition could be established with the open calorimeter in a saturated gap, as exact as that effected with the closed calorimeter in a dry gap. Both systems, at rest under the habitual controls of bath and environmental temperature, functioned for 3 hours,

<sup>18</sup> In this paper the phrase *dry air* will mean not water-free air, but air so far unsaturated with moisture that a temperature fall of calorimetric range will not cause precipitation or supersaturation.

<sup>19</sup> The constancy of temperature was not disturbed by slow stirring which developed no measurable heat but which nevertheless was sufficient to maintain thermal homogeneity; and the occasional warming and cooling of the thermometer stem, which caused temporary displacements, after which the temperature of equilibrium was approached by rising and falling threads, resulted in no permanent change of reading.

<sup>20</sup> It was possible to establish the isothermal condition very quickly by dampening the calorimeter surface, assembling in a dry gap and introducing water into the gap afterward; but this procedure was calorimetrically impracticable, since with subsequent change of temperature, the presence of free water in the gap was a source of thermal disturbance. (P. 935.)

and hence presumably for longer times, as thermostats precise to  $\pm 0.0005^\circ$ . Their behavior under fixed conditions of thermal leakage and under adiabatic change of temperature will be discussed later (pp. 918, 934).

### Heat of Stirring and Stirring Lag

A large number of measurements were made of the heat developed by reciprocating stirring, on account of the very dangerous uncertainties which may result in precise measurement from its incomplete control. Each test was made with the closed calorimeter, which previously had been held isothermal for an hour or more. In all cases the jacket was regulated with such care that the correction for leakage was negligible. Each test lasted from 40 minutes to 2 hours, and none involved variations in stirring speed large enough to make errors in the correction for this irregularity markedly significant. Since all temperature changes observed were slow, it was possible to read the thermometers closer than the usual  $0.0005^\circ$ , and such readings, marked + and -, were taken at 10-minute intervals. The temperature ranges measured were chosen so as to avoid calibration corrections, and check measurements were made at different temperatures. The adequacy of these precautions was not assumed, but was proved in every case by the evaluation of all corrections.

The constancy of the rate of heat production under continuous stirring at identical speeds was first tested by measurements made with different assemblages, scattered throughout the whole series of experiments and over various ranges within a total compass of about  $0.2^\circ$ . It was found that continuous stirring at the constant rate of 56.0 strokes per minute during 30 minutes caused within reading error the same rise of temperature. Since this rate, maintained for this time, will be sufficient in all determinations of heats of reaction in solution to ensure a thorough and rapid mixing, it was thus demonstrated that with systems no more carefully constructed than those here used, mechanical irregularity caused by varying frictional heats developed within the systems would usually have an insignificant effect on the heat of stirring.

The variation of the heat of continuous stirring with change of speed was determined in three systems of widely different internal configurations. The results are given in Table I. The system there marked *Calorimeter A* was that used in the present investigation (See Fig. 1); *Calorimeter S* was a closed thermochemical system closely similar to that used in the determination of the heat of inversion of cane sugar by acid.<sup>21</sup> *Calorimeter R* was one which held between two reciprocating stirrers an electrical resistance enclosed in a loose vertical coil of small metal tubing. In the first two systems the stirring was performed by one stirrer; in the third

<sup>21</sup> Ref. 1, Fig. 1.

TABLE I  
VARIATION OF THE HEAT OF CONTINUOUS RECIPROCATING STIRRING WITH SPEED

Expt.	Duration	Speed	Rate of change in temperature		$\pi$ in. the relation; $R \sim S^x$	Influence on $\pi$ of probable errors of measurement <sup>b</sup>		
			Min. per minute $\frac{\text{Strokes}}{S}$	Degrees per minute $\times 10^6$ $\frac{\text{Degrees}}{R}$		Error of temperature determination $\pm 0.0005^\circ$	Error of stirring rate determination $\pm 0.3$	Sum <sup>c</sup> (maximal)
CALORIMETER A: Temp. range = $.058^\circ$								
175	60	56.2	765	$\begin{matrix} 3.7 \\ 5.2 \end{matrix} > 4.7$	$\pm$	$\pm$	$\pm$	
172	70	42.8	272		0.0	0.2	0.2	
176	90	23.4	12		0.7	0.1	0.8	
CALORIMETER S, Series I: Temp. range = $.036^\circ$								
256	69	56.4	473	$\begin{matrix} 3.7 \\ 8.0 \end{matrix} > 4.9$	$\pm$	$\pm$	$\pm$	
258	55	35.75	89 <sup>a</sup>		0.2	0.2	0.4	
257	55	30.0	22 <sup>a</sup>		0.7	0.5	1.2	
CALORIMETER S, Series II: Temp. range = $.032^\circ$								
263	44	56.8	532	$\begin{matrix} 2.2 \\ 3.9 \end{matrix} > 3.1$	$\pm$	$\pm$	$\pm$	
260	60	45.7	332		0.1	0.0	0.1	
261	60	36.5	138 <sup>a</sup>		0.2	0.2	0.4	
CALORIMETER R: Temp. range = $.035^\circ$								
288	79	55.5	254	$\begin{matrix} 4.3 \\ 4.7 \end{matrix} > 4.5$	$\pm$	$\pm$	$\pm$	
289	80	45.6	109		0.3	0.2	0.5	
290	80	36.2	37		0.8	0.2	1.0	

<sup>a</sup> Maximal values.

<sup>b</sup> Calculated for maximal influence, as affecting the smaller value in each comparison.

<sup>c</sup> The total error is probably less than twice this sum. Lateral displacements of the stirrer were slight, the length of stroke was invariable within 1 mm. (in 50 mm.), and the temperature range was too small to involve significant changes in viscosity, in every series. Certain duplicate measurements indicated that this estimate is too large.

<sup>d</sup> The omitted experiments in each continuous series were tests of the maintenance of the isothermal condition.

<sup>e</sup> The discrepancies between the rates of temperature change at corresponding speeds were due to differences in heat capacity, length of stroke, and mean temperatures, as well as to differences in the internal configurations.

by two stirrers in opposition. The heat developed in the first two systems was about the same; it was considerably less in the third system, in which more eddying occurred. Each group of measurements was made at one time with the same assemblage. It is evident from the data that at low speeds in all cases, the heat developed varies as the fourth and higher powers of the speed; and that with the two simpler systems certainly, and probably with the third, as the rate decreases, the heat developed falls off more rapidly. This variability is shown to be real by the calculated values in the last column of Table I, which exhibit the influences of the maximal probable errors of observation upon the determined index of variability; for if these errors be applied as corrections in the most unfavorable sense the magnitudes of the indices and their quanti-

tative relations are not greatly disturbed. The sense of the change in variability, moreover, is supported by the results of former observation according to which, at higher rates, the heat developed varies as the cube and higher powers of the speed.<sup>22</sup> The data further show that differences in internal configuration may have an effect upon these relations which in precise measurement cannot be safely ignored. The extraordinary sensitivity of heat production to change of speed here shown emphasizes also the need of maintaining with synchronous motors and gear transmissions or similarly effective controls, a measurably uniform speed in all continuous stirring; or else of observing the stirring speed at frequent intervals during measurement and of correcting for its variation. Finally the results prove that at speeds no greater than 12 strokes a minute in systems similar to those here employed (in which friction is comparatively large), the heat developed in 10 hours will be inappreciable by mercury thermometry. Since this rate will be sufficient to maintain thermal homogeneity in all reacting media not distinctly heterogeneous and rapidly changing, it is therefore evident that effective continuous stirring is permissible, even in protracted calorimetry.

In the preceding thermochemical determinations, which necessitated rapid continuous stirring during an initial period of mixture, and which yet demanded the development of very little stirring heat altogether, the reacting system, after solution was complete, was stirred intermittently at the initial rate by groups of strokes applied at 10-minute intervals. This method would be advantageous in many cases, especially when stirring at different speeds would be inconvenient; and similar intermittent stirring at a slower rate would always be preferable to continuous stirring when very small temperature changes were measured, or in very protracted determinations. It had been shown<sup>23</sup> that in homogeneous reacting liquids under adiabatic conditions such stirring, even when very slight, was sufficient to maintain a uniform calorimeter temperature during the progress of any slow reaction; and it was believed that, in the determinations referred to, the slight heat developed by this stirring was estimated with sufficient precision by assuming that the heat per stroke developed by continuous and intermittent stirring at the same rate was the same. This assumption, which left out of account the initial and final effects of liquid inertia, required confirmation. With the two calorimetric systems A and S (p. 909) it had been observed that after stirring at the maximal rate of 56.0 strokes per minute, noticeable motions of the liquid persisted for more than 2 minutes after stirring ceased.<sup>24</sup> The procedure

<sup>22</sup> White, *THIS JOURNAL*, 40, 1880 (1918). Richards and Burgess, *ibid.*, 32, 448 449 (1910).

<sup>23</sup> Ref. 1, p. 1934.

<sup>24</sup> These motions were made apparent in a duplicate system which held a dilute acid-phenolphthalein solution in glass, by the movements of filaments of alkaline solu-



of the tests was suggested by this observation. Three series of measurements were carried out. In the first of these the closed calorimeter was used in a wide air gap, and was left unsealed, so that a slow evaporation took place which, with minimal stirring under the customary controls of bath and environment, caused a measurably constant fall of temperature. Against this fall the rise due to heat of stirring was developed. The stirring speed was constant, and the stirring was both continuous and intermittent, a definite number of strokes being applied at 5-minute intervals in measurements of the latter sort. The measurements were of varying duration and were made and repeated in irregular succession. In the second series this procedure was repeated with the sealed calorimeter, which, with minimal stirring under the same conditions, remained at constant temperature. It is clear that in these two series, the same rates of temperature change—in particular the minimal rates, which were most liable to error—were developed by different rates of stirring, and the experimental uncertainties, consequently, greatly reduced by a comparison of results. A further check upon the precision of measurement was provided by the practice of stirring by groups of strokes of varying duration at equal intervals, since in a given time all such stirrings involved the same end effects but caused different rates of temperature change. The two sets of data (Series I and II of Table II) are closely consistent, and prove that within the thermometric reading error, and for 10 to 20

TABLE II  
HEATS DEVELOPED BY CONTINUOUS AND INTERMITTENT STIRRING AT THE SAME SPEED

Expt.	Duration	Successive strokes in 5 minutes	Total number of groups of strokes	Experimental values: Rates of change in temp. °C. $\times 10^6$		Normal values: Rates of change in temp. °C. $\times 10^6$		Divergence from normal: Rates of change in temp. °C. $\times 10^6$		Corresponding error of observation
				Per min.	Per stroke	Per min.	Per stroke	Per min.	Per stroke	
Min.										
°C. $\times 10^4$										
SERIES I										
87	45	285 (Continuous)	..	578	10.1	578	10.1	±0	±0	
88	50	60	10	126	10.5	124		+2	+0.4	+2
91	50	60	10	105	8.8	124		-9	-1.3	-7
89	60	30	12	65	10.8	62		+3	+0.7	+2
90	60	15	12	33	10.9	31		+2	+0.8	+1
93	45	15	9	35	11.7	31		+4	+1.6	+2

tion, which were produced when a drop of sodium hydroxide solution was placed, directly after stirring had ceased, on the surface of the acid. An immersed centimeter scale exhibited the minimal rates of liquid motion. This simple device served equally well to show the directions of the more rapid currents and their relative rates of retardation in different parts of the system.

## SERIES II

142	65	280 (Continuous)	..	687	12.3	686	12.3	-1	±0	±0
145	65	280 (Continuous)	..	686	12.3	686		±0	±0	
149	60	60	12	133	11.5	147		-14	-8	±13
143	75	30	15	60	10.0	74		-14	-2.3	-7
146	100	30	20	76	12.2	74		+2	+0.1	±0
147	75	.15	15	37	12.2	37		±0	+0.1	±0
148	120	8	25	12	7.3	20		-8	-5.0	-10

## SERIES III

293	50	280 (Continuous)	..	580	10.4	581	10.4	-1	±0	±0
296	50	280 (Continuous)	..	582	10.4	581		+1	±0	±0
294	180	16.7 (10 in 3 min.)	60	40	12.0	35		+5	+1.6	+9
297	200	16.7 (10 in 3 min.)	67	37	11.1	35		+2	+0.7	+4

\* For *normal values*, parts of the rates of change for continuous stirring are taken, proportional in every case to the relative numbers of strokes applied in unit time (5 minutes). The divergence of the experimental and normal values thus measures the divergence of the determined heats of intermittent stirring from strict proportionality to the corresponding heats of continuous stirring.

<sup>b</sup> The *error* values here represent in each case the temperature difference which would, under the conditions of determination, occasion the divergence observed. They were calculated from the extended data of measurement, which are merely summarized here.

\* Determinations 92 and 144 of the continuous series were interpolated tests of leakage constancy and isothermal condition respectively.

The measurements of all series were made in the succession indicated by their expt. numbers: those of Series I on one day; those of Series II and III on two successive days. The differences between corresponding absolute values in the three series is due to slight differences of construction in the systems used, to constant error in the estimation of evaporation leakage in Series I, and to the omission of certain constant corrections in Series I and II. Since Series II involved two assemblages, it is clear that no error entered as a result of mere readjustment of the system.

The measurements most affected by capillary friction were those of Expts. 89 and 148. It will be noted that these exhibit no unusual divergence from the normal. The only divergence which suggests that liquid inertia has a measurable effect is that of Expt. 149; but the correspondingly large negative divergences of Expts. 91 and 143 deprive this result of any significance.

groups of strokes, the average heat per stroke developed by intermittent and continuous stirring is the same. The thermometric precision during slow changes of temperature having been established by these preliminary experiments, two determinative tests were finally made, each of 3 hours' duration (Series III of Table II), in which groups of 10 strokes were applied at 3-minute intervals. These yielded a heat per stroke so close to that determined for continuous stirring as to ensure the absence of sig-

nificant error in correcting for the heat of intermittent stirring developed according to former practice in 10 hours, on the basis of the original assumption.<sup>25</sup> It was thus demonstrated that in protracted adiabatic measurements with homogeneous systems, intermittent stirring is permissible as a valuable alternative practice, advantageous whenever it is desirable to reduce the stirring heat to the least possible magnitude.

Under adiabatic conditions, a minimal effective intermittent stirring can always be determined by trial readings of temperature taken directly before and directly after the stirring is applied. Under merodiabatic conditions, such tests always reveal a considerable lag even when the thermal head is small. This lag, which is obviously occasioned by temperature differences between the interior and the periphery of the calorimeter established by leakage during the intervals of quiescence, is a source of possibly dangerous error in measurement, since because of it the established head is variable and its mean value always less than that observed. It seemed desirable to determine a limit of toleration for possible irregularities of behavior thus occasioned when in adiabatic practice accidental bath heads are established through temporary loss of control. The closed calorimeter surrounded by air gaps 10, 20, and 40 mm. wide was subjected under each of these conditions to bath heads of  $0.6^{\circ}$  and  $1.00^{\circ}$  both higher and lower, which were consistently maintained by the bath drips constant within the same limits of precision as those of adiabatic measurement.<sup>26</sup>

The experimental procedure was identical with that of the leakage measurements, which is fully described elsewhere (p. 920) but it was probably more exact, for the thermal effects measured were so small that excessive precautions had to be taken to determine even the sense of their variability. Under each condition of measurement the thermal leakage

<sup>25</sup> This proportionality will obtain only when the stirring is sufficiently thorough. In parallel tests with other systems, it was found that when any large volume of liquid was left untraversed by the stirrer the normal flow was not established even by 20 strokes of vigorous stirring. This was shown by the initial rates of temperature change, which in one case were less than normal for over 2 minutes, although in this time a thorough mixing was accomplished (Ref. 24). In these cases the heat per stroke in intermittent stirring may be very much less than that of continuous stirring at the same rate. This is advantageous, of course, if the heat developed is negligible: otherwise with every system used the conditions of proportionality should be established by trial.

<sup>26</sup> It seems probable that, when by proper means convection leakage is eliminated, highly accurate determinations may be made under a *condition of constant leakage* thus maintained. All of the leakage measurements here described are instances of such determination. The advantageous applicability of this condition to other than strictly calorimetric measurement, to the measurement of the thermal conductivity of gases and other thermal insulators, for instance, is obvious (cf. Ref. 41, third paragraph). It provides also promising opportunities for the development of precise and adequate procedures in isothermal calorimetry, which are at present under investigation in this laboratory.

was determined; first, when the stirring was continuous at a speed which was found to be completely effective in maintaining thermal homogeneity at all times (about 24 strokes a minute),<sup>27</sup> and second, when stirring was intermittent and slight, at the rate formerly used in thermochemical measurement (10 strokes every 10 minutes at a speed of about 56 strokes a minute). The results are given in Table III. The data show that the

TABLE III  
EFFECTS OF THERMAL INHOMOGENEITY UNDER INTERMITTENT  
STIRRING ON CALORIMETER LEAKAGE

Expts.	Duration	Gap width	Head of bath	Leakage		Difference (A - B)		Average corrections
				Degrees per min. $\times 10^5$				
				With slight intermittent stirring at 10m. intervals	With slow continuous stirring	Degrees per minute	Per cent. of B	
				A	B			
265, 266	50, 40	10	-1.00	-271	-282	11	4.0	4
270, 271	45, 41	10	-1.00	-276	-283	7	2.5	
267, 268	40, 62	10	-0.60	-160	-178	18	10.7	8
273, 272	40, 40	10	-0.60	-164	-175	11	6.5	
276, 277	60, 40	20	-1.00	-169	-180	11	6.3	6
281, 280	85, 60	20	+1.00	+170	+179	9	5.1	
285, 284	50, 40	20	-0.60	-102	-119	17	14.2 <sup>a</sup>	8
282, 283	52, 50	20	+0.60	+ 99	+101	2	2.0 <sup>a</sup>	
226, 225	61, 70	40	-1.00	-170	-183	13	7.1	9
234, 235	50, 50	40	-1.00	-165	-186	21	11.3	
245, 246	61, 80	40	-1.00	-159	-177	18	10.1	
238, 237	60, 80	40	-0.60	- 91	- 96	5	5.2	8
248, 247	50, 70	40	-0.60	- 89	-100	10	10.0	
254, 253	61, 56	40	+0.60	+ 86	+ 96	10	9.6	

<sup>a</sup> Discrepancy traced to faulty insulation: the error is greater in the measurement under negative head, and the average is probably too low.

<sup>b</sup> The percentage corrections are taken in the probable ratio least favorable to an accentuation of the reverse curvatures of the leakage curves (cf. Table V).

thermal effect of the inhomogeneity under minimal intermittent stirring with the 40mm. gap system was proportional to the thermal head, but that with the 20- and 10mm. systems, it increased somewhat less rapidly than the head. The maximal and minimal effects were such as to cause respectively

<sup>27</sup> With the system here used held under a constant bath head of 1°, the measured rates of temperature change [corrected for a heat of stirring as determined under adiabatic conditions (Table I)] were identical when the rates of continuous stirring were 15 and 24 strokes per minute.

about 8% and 4% diminutions of the leakages, which would imply about the same percentage diminutions of the actual thermal heads. The effects of measurement error in these determinations is indicated in the table: although relatively large, they seem not to affect the validity of the above inferences, and the systematic errors involved are in comparison quite negligible. It thus appears that the inhomogeneity permitted by intermittent stirring will introduce no error into adiabatic measurement even if accidental heads of  $0.1^\circ$  are continuously maintained for 20 minutes or more (cf. Table III) and that it may be adequately though laboriously corrected for, if for any practical reason merodiabatic systems under heads of less than  $1^\circ$  are intermittently stirred. It is obvious, however, that in properly conducted merodiabatic measurement the stirring should always be continuous.

Summarizing the practical results of these stirring experiments, it appears that in protracted adiabatic measurement, slow continuous stirring and intermittent stirring at any convenient rate are equally permissible. Intermittent stirring possesses the obvious advantage of developing less heat, and consequently of introducing into measurement smaller errors due to change of speed. It also diminishes leakage between the calorimeter and the outer environment when reciprocating stirrers are used, and is more convenient in measurements which necessitate a rapid transition from vigorous to slight stirring. With continuous stirring maintained at like speed for the same time these advantages are secured only by synchronous regulation of motor speed and faultless transmission, or by more frequent observations of change in the rate of stirring and a more minute correction for its variability, by more careful insulation and correction for leakage to and from the outer environment, and by the use of devices for quick readjustments of stirring speed, such as stepped pulleys or gear clutches. Intermittent stirring is therefore safer, excepting when elaborate and smoothly working mechanisms are available for speed control and, when stirring is reciprocating, for the regulation of outer environmental temperatures; or unless with continuous stirring a lower speed is effective. Experience suggests that, all things considered, a continuous stirring under precise control is preferable for exact protracted adiabatic measurement, unless the reaction period exceeds 10 or 12 hours, or unless the total change of temperature is very small. Under the latter conditions, slow intermittent stirring, which may be so conducted that negligible heat is developed even in very protracted measurement, appears to be advisable.

### **Direct Leakage between Calorimeter and Outer Environment**

By approximate calculation from the known dimensions and thermal conductivities of those parts of the present system which passed directly

from the calorimeter to the outside air, it was estimated that its leakage into an outer environment  $1^{\circ}$  higher would be about 0.30 gram-calorie per hour, corresponding to a temperature change of  $0.00023^{\circ}$  per hour, per degree thermal head. This leakage, if not corrected for, would cause in a measurement of 10 hours' duration, conducted at a mean environmental temperature  $1^{\circ}$  higher or lower than the calorimetric, a constant error of  $0.002^{\circ}$ . It seemed desirable, therefore, to check the none too dependable estimate of its value by actual determination.

Since it was intended always to eliminate this leakage, rather than to correct for it, its maximal value alone was sought; and for this reason the less effectively insulated open calorimeter was used for the tests. The system was first brought to equilibrium close to  $20^{\circ}$  under the usual controls, and the heat of continuous stirring at the maximal rate of 56 strokes

TABLE IV  
DIRECT LEAKAGES FROM CALORIMETER TO ENVIRONMENT

Expt.	Duration	Mean Calorimeter Temp.	Mean Environmental Temp.	Mean head of environment	Leakage Rates		Leakage Coefficients.	
					Degrees per hour $\times 10^4$		Degrees per hour per degree head $\times 10^5$	
	Min.	$^{\circ}\text{C.}$	$^{\circ}\text{C.}$	$^{\circ}\text{C.}$	With minimal intermittent stirring	With rapid continuous stirring	By conduction alone	By conduction and pumping
96	120	19.680	19.87	+0.19	+ 0	...	..	..
97	60	19.675	12.54	-7.14	-21	...	-29	..
98	60	19.694	11.17	-8.52	..	+402	..	-72
99	70	19.773	19.69	-0.08	..	+462	..	..
100	60	19.905	24.87	+4.96	..	+486	..	+48
101	100	19.932	25.26	+5.33	+11	...	+20	..
Mean values:							$\pm 25$	$\pm 60$
Mean leakage by pumping alone:								$\pm 35$

The leakage coefficients for conduction are consistent within measurement error ( $< \pm 0.0005$ ). Those for pumping are not so. The latter effect seems to be accelerated with increase of thermal head, as would be expected.

per minute determined. The temperature of the surrounding air was then brought down to  $11^{\circ}$  and the rate of temperature change within the calorimeter was measured while it was stirred, first very slightly and intermittently and then continuously at the maximal rate. The whole procedure was then repeated with the surrounding air at  $26^{\circ}$ . The data so obtained, corrected for all significant thermal disturbances, are shown in Table IV. They confirmed in a striking (and probably fortuitous) manner the results of previous calculation, and showed also that the environmental

control established (p. 902) was necessary but sufficient to prevent, in measurements made in the determined manner, the introduction of constant error either by conduction leakage or by pumping of air from calorimeter to outer environment.<sup>28</sup>

### Leakage between Closed Calorimeter and Bath

The most instructive of the present measurements were those of thermal leakage through the insulating air spaces between calorimeter and bath. Among them, those least affected by thermal disturbance were measurements made with the closed calorimeter in water-free gaps. The carefully sealed vessel was enclosed successively in dry air spaces 10, 20 and 40

TABLE V  
LEAKAGE BETWEEN CLOSED CALORIMETER AND BATH  
SERIES I  
All Leakage Values in Degrees per Minute  $\times 10^5$

Gap Width Mm.	Thermal Head of bath ° C.	Expt.	Duration min.	Experi- mental values ° C. $\times 10^5$	Experi- mental weighted mean ° C. $\times 10^5$	Extreme varia- tion from the mean ° C. $\times 10^5$	Values determined graphically ° C. $\times 10^5$
All values are $\pm$				All values are $\pm$			
10	0.05	3	70	+ 11	12		{ +12
			70	+ 26			{ -13
	0.10	4	70	+ 26	26	$\pm 0$	{ +26
		9	60	- 26			{ -26
	0.20	6	50	+ 59	55	+4	{ +55
		10	40	- 55			{ -56
		104	40	+ 59			
	0.40	8	40	+116	117	$\pm 1$	{ +117
		11	40	-118			{ -117
	0.60	165	50	+189	184	+5	+184
1.00		163	50	-281	281	$\pm 1$	{ +281
		181	30	-280			{ -281
		182	30	+282			

<sup>28</sup> Leakage coefficients like those of Table IV may be used with convenience to check the accuracy of measurements affected by accidental fluctuations of environmental temperatures. They might, obviously, be used as correction factors, so that the calorimeter could be operated in an uncontrolled outer environment; but this procedure would be less convenient than the use of the controlled environment, and less safe. Even in the case of slow measurements which involve a large change of temperature, the occasional readjustment of the closet thermostat regulator (to keep the environmental temperature always within the permissible range for negligible leakage) will be easier than maintenance of an isothermal environment, and correction for leakage into it.

The smallness of the heat loss which resulted from a very vigorous pumping by the reciprocating stirrers, disposes of the last possible objection to the use of this type of mechanism. It has already been shown that variations in the rate of development of stirring heat caused by mechanical irregularities, which have been assumed to be characteristic of these stirrers, are easily prevented (p. 909). Inasmuch as the reciprocating stirrer possesses many unique advantages in practice (Ref. 1, pp. 1915-1916) its effective insulation, thus demonstrated, is a matter of no small concern.

20	0.10	151	42	+ 18	15	$\pm 3$	$\left\{ \begin{array}{l} +14 \\ -15 \end{array} \right.$
		152	40	- 12			
	0.20	155	30	+ 31	32	+1	$\left\{ \begin{array}{l} +32 \\ -32 \end{array} \right.$
		153	40	- 32			
	0.60	156	30	+110	112	+2	$\left\{ \begin{array}{l} +111 \\ -113 \end{array} \right.$
		154	40	-113			
	0.90	178	43	+169 <sup>a</sup>	175	-6	$\left\{ \begin{array}{l} +176 \\ -174 \end{array} \right.$
	1.00	161	40	+186 <sup>a</sup>	195	-9	$\left\{ \begin{array}{l} +197 \\ -193 \end{array} \right.$
	1.10	179	31	+225 <sup>a</sup>	216	+9	$\left\{ \begin{array}{l} +219 \\ -213 \end{array} \right.$
		180	40	-213			
40	0.10	14	58	(+ 4) <sup>b</sup>	11	$\pm 1$	$\left\{ \begin{array}{l} +10 \\ -12 \end{array} \right.$
		19	50	+ 12			
		24	40	- 10			
		64	50	+ 10			
		102	40	+ 10			
		18	50	+ 16			$\left\{ \begin{array}{l} +16 \\ -19 \end{array} \right.$
	0.15	15	40	+ 30	25	+5	$\left\{ \begin{array}{l} +24 \\ -26 \end{array} \right.$
		20	40	+ 30			
		25	60	- 25			
		65	40	+ 27			
		30	40	+ 46			$\left\{ \begin{array}{l} +39 \\ -41 \end{array} \right.$
	0.20	16	50	+ 56	57	+5	$\left\{ \begin{array}{l} +56 \\ -58 \end{array} \right.$
		22	40	(+ 50) <sup>c</sup>			
		26	50	- 60			
		67	43	+ 61			
		103	40	+ 58			
		139	60	+ 62			
	0.60	21	40	+ 92	97	-5	$\left\{ \begin{array}{l} +96 \\ -87 \end{array} \right.$
	0.80	28	70	+143	142	+4	$\left\{ \begin{array}{l} +143 \\ -142 \end{array} \right.$
		33	40	-142			
		140	60	+146			
		27	40	+197			$\left\{ \begin{array}{l} +194 \\ -194 \end{array} \right.$
	1.00	34	50	-194	194	+3	
		29	38	+244			+250

\* A comparison of the experimental values and those graphically determined will indicate the degree to which the curves were "smoothed out" in plotting. The weighted mean was found by a critical examination of all immediate data; and excepting where single points were but once determined, without reference to the curve. It will be seen that the values graphically determined agree very well with the weighted mean values. Each extreme variation from this mean therefore, is greatly in excess of the probable error.

<sup>b</sup> This value shows a result of capillary friction.

<sup>c</sup> These values were all affected by large calibration corrections which changed the values to which they were applied by amounts about twice as great as the usual divergences between them here recorded. Of these, Nos. 161, 178 and 179 were also affected by time reading errors.

The bracketed values were not considered in reading variations from the mean.

Expts. 64, 65 and 67 were made with an initially saturated air gap, which contained, however, no free water. The measurements were made with various assemblages in which the calorimeter surfaces were at times highly reflecting, at others perceptibly dull, between January 8 and May 10, 1921.



mm. wide; and with each of these, the thermal leakage under several constant heads between  $\pm 0.05^\circ$  and  $\pm 1.20^\circ$  (cf. p. 914) was determined for intervals of from 30 to 120 minutes.<sup>29</sup>

The complete data are given in Table V, and the corresponding leakage curves in Fig. 3. It is apparent that convection here causes a surprisingly small divergence from Newton's law, even with the widest gap under its greatest temperature gradient, and that this is the same for leakage in both directions. It follows at once that with the closed calorimeter all these gaps, even the widest, may be safely used in any adiabatic determination<sup>30</sup> conducted according to the procedure already adopted, even under rough control.<sup>31</sup> But another consequence is of much greater

<sup>29</sup> The most precise determinations were made in groups of 4 to 8, always preceded and followed and occasionally interrupted by hour-long tests of the behavior of the system under isothermal conditions, and were thus proved to be unaffected by any influences other than the thermal heads. The results so obtained were checked by separate measurements scattered throughout the whole period of experimentation; which showed not only that the original procedure involved no accidental errors of any consequence, but that the surface changes incident to long-continued manipulation were insufficient to affect the constancy of radiation leakage for a given head.

In the first determinations, the calorimeter, for lack of adequate mechanisms for stirring speed control, was stirred intermittently; and correction was subsequently made for the small errors of lag thus introduced, by later and very precise determinations in which, under conditions otherwise identical, stirring was both intermittent and continuous (p. 914). The results of these later measurements are given in Table III, but not in Table V, since because they were carried out with a reconstructed and replated calorimeter, they were not strictly comparable with the preceding. Considered as a separate set of values, their relations are in complete accord with those of Table V.

In a few measurements the calorimeter was imperfectly sealed and showed evaporation leakages in the equilibrium tests, which were nearly constant for any group of determinations and were thus safely corrected for. In all measurements temporary irregularities were detected, and all errors of transmission lag were quite eliminated by determining the partial leakage rates at 10-minute intervals and by selecting for record only those ranges over which the flow was constant within thermometric error. The careful selection of well determined end temperatures (Ref. 4), the checking of suspected results by calculation of leakage over overlapping segments of the total range, and the fixing of initial and final temperatures by two or more readings at 1-minute intervals, often reduced thermometric error closely to the least personal error of observation; while the duration of the measurements made its influence upon the precision as small as was desirable or practical. The calibrated temperature readings were invariably corrected in ten-thousandths of a degree for stirring heat, for excess leakage between calorimeter and bath, for leakage to and from the outer environment, and for exposure of the thermometer threads. The sum of these corrections rarely exceeded  $0.001^\circ$ , and thus included no significant errors. Time-reading errors were negligible excepting in measurements of the greatest leakages.

The aggregate temperature range was  $19.3^\circ$  to  $20.5^\circ$ . Within this range, as duplicate determinations showed, change of mean temperature had no measurable effect.

Throughout the whole series there was no evidence of exceptional behavior.

<sup>30</sup> A fact predicted by White 3 years ago [THIS JOURNAL, 40, 388 (1918)].

<sup>31</sup> Ref. 1, p. 1920ff. The present curves show that with the wider gaps the leakage

practical importance. The leakage through the widest (40 mm.) gap is so very small that with it, if the outer environmental and bath temperatures be made to fluctuate with fair regularity, respectively within

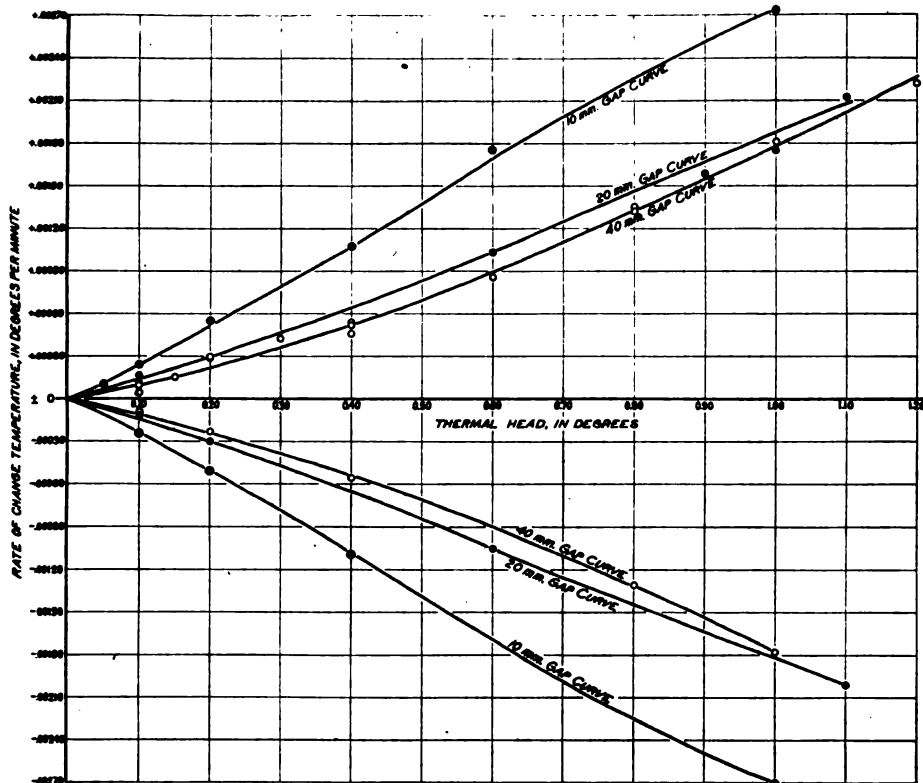


Fig. 3.—Thermal leakage between closed calorimeter and bath: relation to thermal head.

$\pm 0.02^\circ$  and  $\pm 0.01^\circ$  of the calorimetric temperature, it is possible to maintain for hours a condition which with respect to final leakage effect is equivalent to strict adiabaticity.<sup>32</sup> It is not necessary, however, to maintain measurably proportional to thermal head for bath fluctuations as great as  $\pm 0.10^\circ$ . The influence of the heat capacity of the air gaps and of all transmission lags is negligible (see Refs. 16, 17).

<sup>32</sup> Under a head of  $0.2^\circ$  continuously maintained, leakage to or from the outer environment will approximate, with assemblages similar to that here used, 0.6 gram-calorie in 10 hours (Table IV and Ref. 11), and under a constant bath head of  $0.01^\circ$ , leakage through the jackets will be, in the same time, 8.2 gram-calories (Table V, etc.). In the present experiments the corrections for this aggregate leakage effect during 1 hour or more were repeatedly reduced to 0.2 gram-calorie and often to less than 0.1 g.-cal. by maintaining fluctuating external temperatures. With calorimetric systems of 1000 g.-cal. units capacity, this leakage corresponds to a temperature change of not more than  $0.0002^\circ$ . There is no reason why it should be much greater during longer periods of time.

tain such careful control; since, even if only ordinary precautions be observed, the leakage will surely be less than one calorie, and the errors of its estimation quite negligible. Of nearly equal interest is the relation shown by these curves between total leakage and gap width. This is brought out more clearly by the graph of Fig. 4. The effectiveness of the air insulation increases less rapidly for a given increase in width as the gap becomes wider, in such wise that optimum insulation for small thermal heads is practically reached at the 40mm. gap width. It is

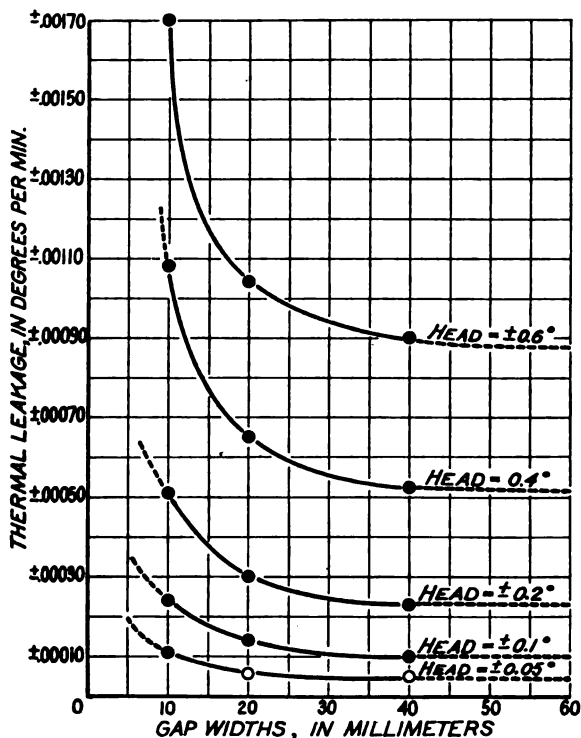


Fig. 4.—Thermal leakage between closed calorimeter and bath—relation to gap width.

clear, therefore, that in adiabatic calorimetry there will be no significant advantage in using gaps of greater widths than this, excepting with very large calorimeters.

An analysis of the several thermal effects involved in this leakage yields interesting results. Of the three factors of thermal leakage, conduction and radiation vary directly as the thermal head (for the small ranges here involved), while convection varies more rapidly. If, therefore, (in Fig. 3) straight lines be drawn tangent to the curves of total leakage at their origins, the ordinate distances between these lines and

the corresponding curves measure the convection leakage. In the present instance, the convection leakages were thus determined, the tangents being drawn through the origins and the determined points at  $0.05^\circ$  head on each curve.<sup>33</sup> It was thus discovered that, while convection over the whole range measured increased more rapidly than the thermal head, the rate of increase in all cases diminished with increase in head. The initial rate of increase was smaller and the rate of its diminution was greater, the smaller the gap width. This general behavior, hardly perceptible to the eye in the curve for the 40mm. gap and in the first half segments of the other curves, is clearly apparent in the curve for the 10mm. gap, which shows distinct reverse flexure at about  $0.6^\circ$  head and becomes parallel to its tangent a little below  $1.0^\circ$  head. The reversal of the 20mm. gap curve occurs at a head somewhat beyond  $0.6^\circ$  and is less marked. It may be presumed that the 40mm. gap curve would show similar flexure beyond  $1.2^\circ$  head. Thus, with increase of thermal head, the curves of the several gaps diverge less and less. An interesting consequence of this behavior is that at about  $1.0^\circ$  head, the total leakage through the 20mm. and 40mm. gaps is the same (Fig. 3). The quantitative relations are shown in Tables VI and VII.<sup>34</sup> From Table VI it is apparent that with the 40mm. gap, convection varies over nearly the whole range as the square of the thermal head, exactly within measurement error; but that with the 10- and 20mm. gaps, it varies respectively as the mean 1.4 and 1.8 powers of the head. The relations of convection leakage to gap width are better shown in Table VII. It is there made evident that at small heads the convection tends to decrease, while at greater heads it increases with increase in gap width. Broadly speaking, at  $0.2^\circ$  head the convection varies inversely as the square root, and at  $1.0^\circ$  head directly as the  $2/3$  power of the gap width; and the data indicate that at greater heads the convection varies with an accelerated rate of change as higher powers of the gap width. With reference to previously determined leakages under greater thermal heads than

<sup>33</sup> The curves were all measurably linear up to this head. When tangents were constructed through points  $0.0001^\circ$  lower on the  $0.05^\circ$  ordinate, they stood away from the curve and were perceptibly too low; and when they were drawn with half this divergence (the probable error of construction), the essential relations hereafter summarized were not significantly affected. (Tables VI, VII and VIII.).

<sup>34</sup> In the calculations, the convection leakages were all corrected for variation of the actual air gap widths from exact dimension, on the basis of the relations exhibited by the actual data (Table V) and in accordance with the assumption that convection per unit effective area was twice as great in the basal as in the lateral gaps. Cf. White, Ref. 35, p. 755. This correction involved necessary assumptions, especially with respect to the magnitudes of the convections from the vertical surfaces; but when these were such as to make the corrections maximal, the original values were not affected beyond the range of possible experimental error. The corrections of convection leakage for dimension were thus considered negligible.

TABLE VI  
CONVECTION LEAKAGE BETWEEN CLOSED CALORIMETER AND BATH: RELATION TO THERMAL HEAD

Series I		All leakage values in degrees per minute $\times 10^5$									
Mm.	Thermal head $H$ $^{\circ}\text{C.}$	Curve ordinates: total leakages		Tangent ordinates: Observed conduction and radiation leak- ages		Conduction and radiation leakages corrected for varia- tion of systems from exact dimensions		Adjusted convection leakages [ $L = (Cd + R)_{corr.}$ ]		$\alpha$ in the relation: $Cv_1 \sim H^x$	
		$L^s$	$(Cd + R)^s_{obs.}$	$(Cd + R)^s_{corr.}$	$Cv_1$	$\alpha$ in the relation: $Cv_1 \sim H^x$		$\alpha$ in the relation: $Cv_1 \sim H^x$		Theoretical convec- tions ( $C \sim H^3$ ) deter- mined for separate segments	
10	0.10	26	24	25	1	1.58		1.87		1	3
	.15	40	36	37	3					4	6
	.20	55	48	49	6					6	12
	.25	70	60	62	8					24	11
	.30	85	72	74	11					18	32
	.40	117	96	99	18					72	26
	.50	149	120	123	26						104
	.60	184	144	148	36						
	.80	239	192	197	42						
	1.00	281	240	246	35						
										Divergences of Actual from theoreti- cal convections $Cv_1 - Cv_2$ $\times 10^5$	
										+2	
										-6	
										-1	
										-6	
										-8	
										-30	
										-69	

[illegible]

\* The total leakage values are affected by corrections for intermittent stirring lags (cf. Table III). If these be not applied, the relative values of  $\kappa$  above will be the same as those determined on the assumption that the lag is proportional to thermal head, and will have the following successive values: For the 10mm. gap: 1.87, 1.50, 1.64, 1.63, 1.37, 0.82; for the 20mm. gap: 2.00, 1.81, 1.74, 1.76, 1.62, 1.37; for the 40mm. gap: 2.12, 2.00, 2.10, 1.97, 1.96, 1.84. The inferences drawn from the data will, therefore, not be affected by doubt in consequence of possible errors in the estimation of lag.

<sup>b</sup> The actual convection leakages here,  $L - (Cd + R)_{\text{act.}}$ , are not recorded. The conduction and radiation leakages determined by the tangent constructions,  $(Cd + R)_{\text{act.}}$ , were corrected for variation from exact dimension (so as to represent this leakage for gaps exactly 10, 20, and 40 mm. wide) on the supposition that conduction was uniform and normal to the calorimetric surfaces. This neglect of "end effects" introduced no significant error into the small corrections; and since the dimensional error had no measurable effect on the convection leakage, the adjusted values of the convection were determined with sufficient precision as  $L - (Cd + R)_{\text{corr.}}$ . The final relations determined apply, therefore, within measurement error to gaps of exact 10, 20 and 40mm. dimension.

TABLE VII  
CONVECTION LEAKAGE BETWEEN CLOSED CALORIMETER AND BATH  
RELATION TO GAP WIDTH

Thermal Head	Gap Width	Convection Leakages [From Table V] Degrees per minute	$y$ in the relation: $Cv_1 \sim S^y$		
$H$ °C.	$S$ Mm.	$\times 10^5$ $Cv_1$	For the 10- and 20mm. gaps	For the 20- and 40mm. gaps	For the 10- and 40mm. gaps
0.20	10	$\pm 6$	-0.59		
	20	4			-0.50
	40	3		-0.41	
0.30	10	11	-0.29		
	20	9			-0.31
	40	7		-0.33	
0.40	10	18	-0.26		
	20	15			-0.24
	40	13		-0.21	
0.50	10	26	-0.24		
	20	22			-0.16
	40	21		-0.07	
0.60	10	36	-0.31		
	20	29			-0.06
	40	33		+0.19	
0.80	10	42	+0.09		
	20	45			+0.16
	40	54		+0.23	
1.00	10	35	+0.70		
	20	57			+0.63
	40	84		+0.56	

\* Figures in italics refer to the adjusted tangent ordinates of the 20mm. gap (Ref. 43).

these,<sup>36</sup> this whole behavior seems sufficiently strange to appear questionable in the absence of complete assurance as to the sufficient precision of the data. When this precision is not too favorably estimated, it appears that the falling off in the acceleration of the convection with increase of head is undoubtedly real; and that the initial diminution of convection with increase of gap width, while not rigorously proved, appears to be probable—or, more definitely, that the absence of any measurable increase of convection with gap width at the smaller heads is certain.<sup>36</sup> The phenomena as a whole suggest that two effects are operative here in retarding the convection, which, if normal, would increase continuously both with thermal head and with gap width. One of these increases with thermal head, and at any given head, is greater in the narrower gap; the other has its greatest relative effect when the head is very small, and increases with gap width. The present data are insufficient to support any definite statement as to their probable causes.<sup>37</sup> It suffices to remark the fortu-

<sup>36</sup> White, *Phys. Rev.*, 10, 750-751 (1917).

<sup>37</sup> The probable error of each determined leakage is not greater than  $0.001^\circ$  in 50 minutes, or  $0.00002^\circ$  per minute. This value, which is twice the thermometric reading error, and approximates that of temperature range determination, might in this case be assumed *a priori*. It is, however, vouched for by the concordance of duplicate measurements for almost every leakage. These show an extreme variability from the mean of from  $0.00001^\circ$  to  $0.00006^\circ$ , which averages  $0.000035^\circ$  per minute for all heads less than  $1^\circ$  (Table V); and their separately weighted averages are confirmed within  $0.00001^\circ$  per minute by the independently constructed curves, which in their smoothing out merely define those possible values for each head which represent a consistent continuous variability of leakage with increase of head.

This measurement error only could make doubtful the variability of leakage with increase of head (Table VI), since error in the determination of the curve tangent is proportional to the head, and the stirring lag correction is certainly proportionally no greater at high heads than at low. If it be applied to the convection leakages of the two narrower gaps so as to produce in each case its maximum possible effect in compensating the observed diminution of convection rate with increase of head (*i. e.*, if in each case it be added to the greater and subtracted from the less of the convection rates at high and low heads) this diminution persists in the 10mm. gap leakage, and is on the average barely compensated in the 20mm. gap leakage.

An analogous application of the maximal measurement error to the determined variability of convection leakage with increase of gap width (Table VII) results in an exact compensation of the observed diminution at  $0.4^\circ$  head. At greater heads, obviously, the effect is less: at smaller heads it is indeterminate, since the leakages themselves are of similar magnitude and are highly uncertain; although the dependability of their approximate relations is vouched for by the general consistency of the complete data. This variability, therefore, is also unaffected by error of observation. The possibility of its invalidation by error in the tangent constructions (which define independently for each gap the mean convection leakage) is shown further on to be negligible (Ref. 42).

It thus appears almost certain that both variabilities are real.

<sup>37</sup> The phenomena appear less extraordinary, however, if possible causes be imagined. The first effect might result from a retarding turbulence caused by the con-



nate circumstance that both effects are calorimetrically advantageous, since they obviously occasion the small divergence of the total leakage relations from Newton's law already noted.

Simultaneously with the convection leakage, that of radiation and conduction together had been determined. To separate these two leakages it was necessary to estimate that of conduction. Since there is no convenient mathematical procedure for such determination in the case of completely enclosed systems, the conduction leakage was found experimentally. Advantage was taken of the fact that the distribution of temperature throughout a space bounded by two closed isothermal surfaces is similar to the distribution of potential within the same space bounded by equipotential surfaces.<sup>38</sup> It follows from this that for any particular system, the heat flow for the one condition is proportional to the electric force for the other, at any point; and that the total heat flow between the isothermal surfaces is proportional to the electrical capacity of the same system used as a condenser. For the calorimetric system, therefore, the heat conduction per degree temperature head is  $4\pi Ck/K$ , where  $C$  is the electrical capacity in centimeters,  $K$  the dielectric constant ( $= 1$  for air, as in the present case) and  $k$  the thermal conductivity (in the present case  $= 0.000058$  for air at  $20^\circ$ );<sup>39</sup> the factor  $4\pi$  being necessary to reduce the electrical capacity to equivalent units.<sup>40</sup>

The electrical capacity of the present 40mm. gap system (that in which the "end effects" were greatest) was determined in the radio laboratory of Columbia University by the method of substitution in a resonant circuit loosely coupled with a high frequency generator. It was found to be 24 micro-micro farads or 21.5 cm.,<sup>41</sup> and yielded the value 0.0156 gram-figuration of the gap, which is more than slightly modified by the presence of the necessary chimneys and supporting frame of the calorimeter. Such turbulence would be likely to be greater at greater heads and in the narrower gaps. The second effect might be caused by irregular distribution of heat on the jacket wall. This would occasion slight convection currents roughly parallel to the surfaces, which would tend to cause a general drifting of air across the normal stream lines. Its effect would be noticeable only in gaps of sufficient width, but would be compensated by the increase of normal convection with increase of gap width; and since it would be independent of the head, it would be noticeable only under small heads. A like effect might perhaps be produced by protracted transmission lags, which would be greater at smaller heads and in wider gaps, but which would be similarly compensated.

<sup>38</sup> This of course is a special instance of a more general analogy.

<sup>39</sup> E. Mueller, *Wied. Ann.*, 60, 82 (1897).

<sup>40</sup> This relation is very clearly seen in the simple case of a system of two parallel areas on infinite plane surfaces. Here, heat conduction per degree temperature head  $= (A/d)k$ , and electrical capacity  $= (A/d)K + 4\pi$ , where  $A$  is the area of each surface and  $d$  the distance between the two (in centimeters); whence the heat conduction per degree temperature head  $= 4\pi C$  ( $^\circ/K$ ) (calories per second, when  $C$  is the capacity in centimeters).

<sup>41</sup> The separate measurements made with different dispositions of the internal leads

calorie per second, corresponding to  $0.00076^\circ$  per minute for the conduction leakage, and  $0.0070$  gram-calorie per second, or  $0.00034^\circ$  per minute for the radiation leakage. This radiation leakage, assumed to be the same in every measurement made under  $1^\circ$  head and to vary like the conduction proportionally with the head, then yielded the complete series of conduction leakages; and in combination with the other data of measurement, the ratios of convection, conduction and radiation leakage under all of the established conditions. The complete data are given in Table VIII.<sup>42</sup> The leakage ratios there given bring out very clearly the calorimetric advantage of the wide (40mm.) gap. With this gap the conduction leak-yielded the values 25.0, 24.0, 23.3, 24.4 m.m.f. The accuracy of measurement seems to be considerably better than 5% and might, without doubt, be improved, were a closer approximation necessary.

It is clear that the above procedure furnishes a convenient method for determining the thermal conductivity of any closed insulating space, whatever its configuration.

Since the calorimeter here used was of typical form (a cylinder of which the height is about three times the radius) and since the air gaps surrounding it were nearly symmetrical, the data obtained may serve to define an empirical rule for the approximate estimation of conductance in similar systems. The conductance of the 40mm. gap system was 0.93 times, and that of the 10mm. gap system was 0.87 times the conductance of two plane areas on infinite plates the gap width apart, each equal to the total surface of a cylinder having the mean radius and height of the gap surfaces. With close approximation then, the conductance of a closed cylindrical system of the most convenient form (in which the height of the calorimeter is about three times, and the uniform gap width no greater than  $\frac{3}{4}$  of the calorimeter radius) may be very quickly computed with reference to this cylinder of mean dimensions. For all such systems, the conductance

under  $1^\circ$  head  $= 0.9 \frac{2\pi R(R+H)}{d} k$  calories per second, where  $R$  and  $H$  are the mean radius and height of calorimeter and jacket and  $d$  the gap width in centimeters, and where  $k$  is the thermal conductivity of the insulating material.

The writer desires in this place to acknowledge his great obligation to Professors H. W. Webb and J. H. Morecroft for their kindness in arranging for and in carrying out the electrical measurements.

<sup>42</sup> A valuable criterion for the correction of previous estimates of the combined radiation and conduction leakages was provided by the calculation of *minimal* values for the conduction leakages. On the assumption that all conduction was normal to the surfaces, and that it varied, therefore, inversely as the gap width between basal surfaces and inversely as the logarithm of the ratio of gap radii between the lateral surfaces, the minimal conduction leakages for the several systems used were calculated from the actual gap dimensions. They were found to be for the 10mm. gap,  $0.00199^\circ$ , for the 20mm. gap  $0.00112^\circ$  and for the 40mm. gap,  $0.00062^\circ$  per minute. These minimal values were consistent with the experimentally determined leakages of the 10mm. and 40mm. gaps, but not with those of the 20mm. gap (Table VIII). It thus appeared that the tangent of the 20mm. gap curve had been drawn too low. The values of the convection and conduction leakages determined by it were, therefore, corrected, *within possible error of previous estimation* (Ref. 33) by increasing its intercept at  $1^\circ$  head from  $0.00140^\circ$  to  $0.00180^\circ$  per minute; and this having been done, the derived values of the conduction leakages became consistent. These and all corresponding adjusted values are printed

TABLE VIII  
ANALYSIS OF THERMAL LEAKAGE BETWEEN CLOSED CALORIMETER AND BATH  
All leakage values in degrees per minute  $\times 10^6$

Gap Width $S$ Mm.	Thermal Head $H$ °C.	Experimental Values		Radiation leakages ( $Cd + R$ ) <sub>obs.</sub> — $Cd_{obs.}$ $R$	Values Corrected for variation from exact dimensions		Ratios of Leakages $R: Cd_{corr.}: C_n$		Adjusted val- ues corre- sponding to maximum conduction ( $Cd_{Max.} = 0.00060$ at 1° head)
		Conduction and radiation leakages [From Table VI] ( $k_{10} = 0.000058$ ) ( $Cd + R$ ) <sub>obs.</sub>	Conduction leak- ages derived from electrical capacity measurements $Cd_{obs.}$		Conduc- tion $Cd_{corr.}$	Convec- tion [From Table VI] $C_n$	Experimental values	Adjusted values	
10	0.10	24	21	3	21	1	1:6.3:0.3	.....	1:7.1:0.3
	0.20	48	41	7	42	6	0.9	.....	1.0
	0.40	96	82	14	85	18	1.3	.....	1.5
	0.60	144	124	20	127	36	1.8	.....	2.0
	0.80	192	165	27	170	42	1.6	.....	1.8
	1.00	240	206	← 34	212	35	1.0	.....	1.2
20	0.10	14	11	3	10	11 <sup>a</sup>	1:3.1:0.3	1:3.4:0 <sup>a</sup>	1:3.5:0.3
	0.20	28	21	7	21	23	0.6	0.3	0.7
	0.40	56	42	14	42	46	1.1	0.8	1.3
	0.60	84	64	20	62	68	1.5	1.5	1.6
	0.80	112	85	27	83	91	1.7	1.4	1.9
	1.00	140	106	← 34	104	114	1.7	1.4	1.9
40	0.10	11	8	3	8	0	1:2.2:0	.....	1:2.5:0.0
	0.20	22	15	7	15	3	0.4	.....	0.5
	0.40	44	30	14	30	13	0.9	.....	1.1
	0.60	66	46	20	46	33	1.7	.....	1.8
	0.80	88	61	27	61	54	2.3	.....	2.3
	1.00	110	76	→ 34	76	84	2.5	.....	2.8
	1.20	132	91	41	91	118	2.9	.....	3.3

<sup>a</sup> All figures in italics refer to the adjusted tangent ordinates of the 20mm. gap (Ref. 42).

age at all heads is reduced nearly to twice that of the inevitable radiation; while the convection leakage, which remains less than that of corresponding conductions at all heads below  $0.80^\circ$ , becomes negligible below  $0.10^\circ$  head. It follows that in adiabatic practice this air gap provides an insulation almost a third as effective as a perfect vacuum gap, and thus renders more or less illusory any imagined advantage to be gained in adiabatic calorimetry by the use of practicable vacuum insulations.

### Effects of Condensation of Moisture on Calorimeter Surfaces

The regularity in the behavior of the closed calorimeter with respect to thermal leakage, above described, was conditioned by the maintenance of a practically dry gap. The presence of even a small quantity of liquid water in the gap always caused upon closure a rapid saturation, followed by a long-continued rise in the temperature of the calorimeter, which apparently was due to the condensation of water upon it. This effect, the extreme duration of which was unanticipated, was obviously a possible source of very serious error in measurement, and was examined with some care.

The calorimeter jacket cover, which like that of the calorimeter carried extra apertures designed for use in other measurements, was fitted with a glass pipet through which water could be quickly withdrawn from the calorimeter at any time, and with bent tubes through which it could be delivered into the gap without wetting the calorimeter surface, both arrangements being so contrived that excepting during the half minute of manipulation, the calorimeter and gap would remain effectively insulated. The isothermal condition having been maintained for an hour or more, water in quantity insufficient to affect measurably the heat capacity in italics in Tables VII and VIII. It will be seen that they lead to the same inferences as the original data, in all cases (cf. Ref. 36).

By a comparison of the calculated minimal values given above with the corresponding experimental values of Table VIII, it will be evident that the "end effects" occasion about 18% of the whole conduction leakage in the 40mm. gap system, but are negligible with the other systems. It follows that for systems of similar configuration with air gaps no wider than 20 mm., the conduction leakage may be calculated with a precision sufficient for usual purposes directly from the gap dimensions, on the assumption that all lines of heat flow are normal to the gap surfaces.

This conclusion was substantiated, and several errors of previous approximation were checked, by a derivation of the coefficient of conductivity for air at  $20^\circ$  from the adjusted values of the combined radiation and conduction leakages for the 10- and 20mm. gaps, and from the ratio of the corresponding minimal conduction leakages calculated from that of the gap dimensions.

Experimentally, in degrees per minute: for the 10- and 20mm. gaps at  $1^\circ$  head,  $(Cd_{10} + R)_{\text{corr.}} = 0.00246$  and  $(Cd_{20} + R)_{\text{corr.}} = 0.00148$  (Table VIII); whence  $Cd_{10} - Cd_{20} = 0.00098$ . By calculation from corresponding ideal dimensions  $Cd_{10}/Cd_{20} = 0.53$ . Hence  $Cd_{10} = 0.00208$  and  $Cd_{20} = 0.00111$  degrees per minute; and  $k_{20} = 0.000057$ , in both cases.

of the system was withdrawn and quickly transferred to the gap. An immediate rise in temperature was observed, which continued at a practically undiminished rate for an hour, and which, after several hours, was still increasing; it was, moreover, the same whether the bath temperature fluctuated about that of the calorimeter or was held continuously below it. It is clear that this temperature rise could have been due to nothing but superficial heating caused by the condensation of water on the surface of the calorimeter. In the first tests, the calorimeter surface, though fairly clean, was not brightly reflecting. It was later thoroughly cleaned, particular care being taken to remove the last traces of possible hygroscopic contamination and of grease.<sup>43</sup> The test was then repeated: the temperature effect was the same, though diminished. After it had become imperceptible, the surfaces were exposed and allowed to dry by evaporation. Another repetition of the test then yielded the same result. In later trials the dry surface was slightly greased by a very minute quantity of vaseline, and then completely covered with a thin layer of vaseline. The effects were precisely similar, and with the well greased surface were measurably the same as with the cleanest. It was thus made probable that the effect was not due to the presence of chemically reacting or of hygroscopic material on the surface, and that it could not be prevented or significantly accelerated by attempting to reduce the magnitude of the adsorption. Precisely similar effects were observed with the open calorimeter, the surface of which was dry. In a dry gap, its temperature naturally fell as a consequence of evaporation, but when the gap was wetted as in the previous tests this thermal effect was suddenly reversed. With both systems the entire effect was eliminated by wiping the calorimeter vessel all over with a chemically clean damp cloth, allowing it to stand under a bell jar until the surface showed very few adhering drops, and enclosing it in a water-saturated gap. It is not certain that the more rapid evaporation from adhering drops was significant, though the results of one or two measurements indicated this. The possibility of irregularity from this cause would better, however, be thus avoided.

The character and magnitude of these effects are shown in Table IX. These data indicate that very serious errors are likely to occur in calorimetric measurement when dry calorimeter surfaces are placed in wet gaps, and point specifically to the dangerous disturbances which may result from gasket leakage, or from accidental spattering of calorimeter water

<sup>43</sup> The apparently clean surfaces were rubbed and washed with benzene, then with pure soap, scrubbed with clean wet cloths and thoroughly drenched with grease-free distilled water. They were afterward rubbed with chemically clean cloth saturated with alcohol, washed with alcohol, again drenched with water, and dried in dust-free air. The last adhering water film gave no indications of the presence of grease, and the finally dry surface was brightly reflecting and apparently untarnished. The cleaned calorimeter was kept under a bell jar and was invariably handled with a clean cloth.

TABLE IX  
EFFECTS OF CONDENSATION OF MOISTURE ON CALORIMETER SURFACES

Expt.	Condition of calorimeter surface	Rate of initial temp. fall due to evaporation	Rates of temperature change caused by condensation			Total heat of adsorption: roughly calc. from the preceding data (in gram-calories)	
			Initial	After 1 hour	After 2 hours	For whole surface	Per sq. cm.
All in degrees per minute $\times 10^5$							
CLOSED CALORIMETER IN 40MM. GAP							
69	Slightly dull	.....	+32	+18	+6	29.8	0.042
75	Clean and bright	.....	+27	+12	+5	24.8	0.035
76	Clean and bright	.....	..	+ 8	+3	..	...
77	Lightly smeared with vaseline	.....	+25	+ 8	+3	22.6	0.033
78	Heavily coated with vaseline	.....	..	+10	+3	..	....
OPEN CALORIMETER IN 40MM. GAP							
70	Slightly dull	-35	+ 5	+ 3	$\pm 0$	..	....
71	Slightly dull	-20	$\pm 0$	$\pm 0$	..	..	....

during assemblage. Inasmuch as the effect is not only greatest, but is also variable during the first 30 minutes, it is likely to introduce error into the measurement of rapid as well as that of slow changes. The effect of the evaporation of accidental water from a calorimeter surface into a dry gap, and that of the chemical absorption of the gap moisture by hygroscopic substances on the calorimeter surface have been previously commented upon.<sup>44</sup> The present observations appear to show that any accidental water in the gap will occasion significant irregularities of behavior, whether hygroscopic substances are present or not.<sup>45</sup> With the closed calorimeter it is best to keep all gap surfaces scrupulously dry, and in this case it becomes doubly important to make the vessel vapor-tight, inasmuch as, if evaporation occurs, some of the escaped moisture will be deposited on its outer surface. Since the phenomenon is one of

<sup>44</sup> White, *Phys. Rev.*, 31, 575 (1910).

<sup>45</sup> The data of Table IX indicate that even when the calorimeter surface is clean and bright, the total amount of water adsorbed is 0.00006 g. or more per sq. cm. This quantity is very much greater than that observed by White (Ref. 44) to be adsorbed by clean nickel surfaces, and is comparable to the adsorption on tarnished copper which he detected. This large discrepancy cannot be ascribed to the smaller sensitivity of the calorimetric measurements. It is not impossible that the condensations here observed were due in part to very slight contamination, though in view of the precautions taken, (see Ref. 43) this seems unlikely. On the other hand, White's adsorptions may have been incomplete. It is highly desirable that this discrepancy be explained. Meanwhile, the practical consequences of the present observations remain unaffected by any doubt. The calorimeter surfaces in these tests were certainly as clean as very careful manipulation permitted them to be. The phenomena observed, therefore, whether they were due wholly or only in part to the simple adsorption of moisture, may be accepted as characteristic causes of disturbance in any practical calorimetry.

adsorption, such condensation will occur before the gap reaches saturation, and it will reduce the thermal effect of the evaporation in an indeterminable way. With the open calorimeter the only recourse is to wet the surfaces of the vessel in the manner described above and to enclose it in a saturated gap.

### Leakage between Open Calorimeter and Bath

Measurements of leakage were carried out with the open calorimeter in all respects similar to those made with the closed calorimeter. The behavior thus exhibited was so complicated that any description of it sufficiently minute to prove the validity of the inferences drawn from its analysis would probably not be justified by their practical importance. These inferences will, therefore, be only briefly summarized in this place; the evidence upon which they rest, if it ever seems necessary or advisable to present it, will be given in full elsewhere at another time.<sup>46</sup>

With an open calorimeter in a gap initially dry, the thermal disturbances, which are due not only to evaporation into the air gap but also to superimposed effects of surface condensation, are very protracted, and on account of unavoidable small differences in initial temperatures and gap saturations, they are never reproducible either with respect to magnitude or variability with time. Such systems are, therefore, quite unavailable for protracted calorimetry and yield uncertain data even in quickly completed adiabatic measurements unless corrections be made for their variable leakage by careful interpolation from the results of preperiod and postperiod observations. The rates of leakage are, however, nearly enough linear during the first half hour to make the error of such interpolation negligible.

The open calorimeter with invisibly wetted outer surface, enclosed in a vapor saturated gap which holds no free water, exhibits equal or greater variability in the magnitude and character of the initial disturbances, in this case due to unavoidable differences in prior temperatures of calorimeter and bath. If the bath be previously lower, the calorimeter temperature, under conditions which normally establish an isothermal condition, slowly rises; if the bath be previously higher, it falls. Both of these changes are extremely protracted and may be shown to be caused by changes in the densities of the films of water adsorbed by the calorimeter surface. Under bath heads, both positive and negative, the leakage of systems of this type is greater than the corresponding leakage of the closed system through dry gaps of the same width. The excess leakage is probably caused partly by an increased convection rate, but in greater measure by distillation, that which occurs when the bath is at higher temperature being due to a transfer of moisture to the calorimeter from adsorbed films on the jacket walls. These open systems therefore are, like the

<sup>46</sup> Publications of the Ernest Kempton Adams Fund for Physical Research.

preceding, unavailable for protracted measurements, though they may be similarly used in measurements of short duration. Although they involve greater and more variable leakages, they possess the advantage that under bath heads less than  $0.2^\circ$  the leakage is the same in both directions, so that a correction for imperfect adiabaticity may be correctly determined on the assumption that leakage is proportional to thermal head.<sup>47</sup>

When the air spaces surrounding an open calorimeter hold free water, the leakages under both positive and negative bath heads are still further increased, primarily by the effects of free distillation. The phenomena in this case are so markedly affected by the quantity of water in the gap, by its location and distribution and by its influence on the magnitudes and rates of the surface adsorptions, that they exhibit at first glance a hopelessly capricious variability. A rough and partial analysis of these leakages was possible, but beyond furnishing additional data on the adsorption phenomena its only practical result was to prove that the presence of even a small quantity of water in the air gap might well invalidate any calorimetric determination.

As a whole the experiments with the open calorimeter led to the final judgment that although such systems may with proper precaution be used in quickly completed adiabatic measurements, they are unavailable for any other, and excepting for work confined within very narrow temperature ranges, would best be discarded altogether.

### Summary

A. From the results of an extensive series of measurements undertaken to establish a standard of accuracy for the calorimetry of slow processes, it has been determined that in order to attain the accuracy defined by the gain or loss of half a gram-calorie in 10 hours, the following precautions are necessary and sufficient.

1. A closed calorimetric system must be used which allows no measurable evaporation into the insulating air gaps, and these gaps must be dry (unsaturated with water vapor).

2. The outer environment must be thermostatically controlled whenever there are conducting parts which pass directly from the calorimeter into the surrounding air, with a precision characteristic of the system employed. This is about  $\pm 0.2^\circ$  when encased mercury thermometers are used. It is advisable to keep the environmental temperature always close to the calorimetric within the characteristic range of negligible di-

<sup>47</sup> In the preceding research, which was carried out with an open system of this type, this proportionality was observed, and was made the basis of the correction for imperfect adiabaticity. The present measurements confirmed these former observations, and by showing the probable causes of the proportionality, explained their seeming inconsistency with those of other observers, which was noted at the time. (Ref. 1, pp. 1923, 1924.)



rect leakage; and it is necessary to correct for fluctuation beyond this range. A constant temperature closet is requisite for this control. A convenient construction of this sort is described.

3. With the usual system of about 1000 gram-calorie units heat capacity the air gaps should be not less than 40 mm. wide: but there is no practical advantage in using gaps wider than this. The heat capacity of these wide gaps is relatively too small to cause indeterminate errors of measurement. With the 40mm. gap, when the bath temperature fluctuates within  $\pm 0.01^\circ$ , and the environment within  $\pm 0.2^\circ$  of the calorimetric, the system is practically adiabatic within the error above defined, the total leakage, of which the convection factor is negligible, being little more than three times that of a perfect vacuum gap. The leakage rate in such systems is the same in both directions, and for heads below  $0.1^\circ$  is proportional to the head. Correction for imperfect adiabaticity due to bath fluctuation may be made on this basis, since transmission lag has no measurable effect on the leakage. A new type of calorimeter embodying these advantages is described. With this system, the initial conditions are perfectly adiabatic; and the total calorimetric lag for the temperature changes characteristic of long-continued operations is negligible.

4. It is permissible and advantageous to stir the closed system reciprocally. In the installation described, this may be done without significant loss of heat. The heat of stirring is developed identically in different assemblages and at the same rate for any one speed, whether stirring is continuous or intermittent. It may vary at low speeds with the fourth and higher powers of the speed. The continuous stirring necessary to ensure mixture in chemically reacting systems is productive of negligible error; and similar stirring at low speeds throughout determination is shown to be practicable, though in very protracted operations intermittent stirring is the better practice. Strictly uniform speeds are necessary for long continuous stirring, but not for intermittent stirring, nor for continuous stirring during mixture if the approximate rates of heat production under different speeds be known for the system used.

5. The open calorimeter is unavailable in protracted calorimetry; since, even with an initially dry gap, evaporation leakage is inconstant as the result of uncontrollable variability in prior conditions. This is due in great part to the condensation of water vapor in the air gap on the walls of the calorimeter, which occurs on clean as well as on contaminated surfaces, and is probably due to the simple adsorption of moisture, an effect which can be neither eliminated nor controlled even under approximately isothermal conditions. With change of temperature its effects are greater and still more irregular, and in water-saturated gaps are complicated in the extreme.

B. The closed system is best for all types of calorimetry; but in

the adiabatic measurement of swift reactions the open calorimeter may be safely used, either with dry surfaces in an initially dry gap, or with invisibly wetted surfaces in a saturated gap which holds no water, provided always that correction for aggregate thermal disturbances due to evaporation leakage be made by interpolation from the results of observations taken before and after the reaction period. The initially dry gap, with which leakage is less, and more nearly uniform, is preferable in such measurement; but correction for imperfect adiabaticity is safer with the saturated gap.

Under all heads less than  $1^{\circ}$ , the total leakage from a closed calorimetric system in a dry gap shows slight divergence from Newton's law, since the convection increases very slowly with increase in gap width, and varies as powers of the thermal head less than 2 excepting when the gap is unusually wide.

Similar leakage from the open system is irregular, but yields itself to a rough analysis which gives some indication of the character of the thermal disturbances and the magnitude of the uncertainties characteristic of the merodiabatic measurements which have yielded the bulk of our present thermochemical data.

An experimental method for the determination of conduction leakage in any closed calorimetric system is described, and a simple empirical rule for estimating its approximate magnitude in closed cylindrical systems of convenient dimensions is given.

As a whole the work illustrates several applications of an experimental procedure which permits the long-continued maintenance either of an adiabatic condition or of a condition of constant leakage in a system of changing temperature. The latter condition is available for isothermal calorimetry, and for the simplification of method in other types of physical measurement. In illustration of one such application, the thermal conductivity of air, incidentally determined (with no specific precautions) at atmospheric pressure by the analysis of thermal leakage including convection yielded  $k_{20^{\circ}} = 0.000057$ , in close agreement with the accepted value.

Precise data are submitted which quantitatively define the above statements.

In conclusion, the writer desires to express his obligation to the Department of Physics of Columbia University for laboratory accommodations and shop facilities essential to the prosecution of this investigation, and to the University for the Ernest Kempton Adams Research Fellowship Fund, with which the expenses incident to it were defrayed.

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[CONTRIBUTION FROM THE LABORATORY OF PHYSICAL CHEMISTRY OF THE POLYTECHNICAL INSTITUTE OF COPENHAGEN]

## CALCULATION OF THE OSMOTIC AND ACTIVITY FUNCTIONS IN SOLUTIONS OF UNI-UNIVALENT SALTS

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### 1. Introduction

For the theory of solutions it is of the greatest importance to find an expression which, as the concentration approaches infinite dilution, shows a uniform convergence towards an ideal state and is still able to account for the peculiarities of the various salts at higher concentration. For a long time work has been in progress, mostly on an empirical basis, to establish the laws governing the anomalies of the strong electrolytes. A particularly successful research in this line is the critical study of Noyes and Falk<sup>1</sup> who found the osmotic properties of salt solutions to be represented by the well-known equation,

$$2 - i = K\sqrt{c}, \text{ or } 1 - \varphi = \alpha\sqrt{c} \quad (1)$$

where  $\varphi$  indicates the osmotic coefficient<sup>2</sup> and  $\alpha$  a constant peculiar to the salt in question. This equation enabled us to account approximately for the thermodynamic properties of salt solutions within a rather considerable range of concentrations, and with its aid we were in a position to calculate<sup>3</sup> approximately ion activities and solubilities based on the modern view of salt solutions as being completely ionized.

It is obvious, however, that Equation 1 does not fulfil the requirement of a uniform convergence with decreasing concentration, because the function  $1 - \varphi$  which we shall term *the osmotic deviation* is directly proportional to the constant  $\alpha$  peculiar to any salt. When comparing two salts, the equation

$$\frac{(1 - \varphi)_1}{(1 - \varphi)_2} = \frac{\alpha_1}{\alpha_2}$$

evidently holds, even at the greatest dilutions.

In an interesting paper,<sup>4</sup> Lewis and Linhart have proposed the expression

$$1 - \varphi = \alpha c^n \quad (2)$$

in the place of Equation 1 and have shown that this expression conforms very closely to available accurate measurements of freezing-point lowerings. It is not surprising that this expression can be better satisfied than Equation 1 because it contains two independent constants  $\alpha$  and  $n$  to be varied when

<sup>1</sup> Noyes and Falk, *THIS JOURNAL*, 32, 1011 (1910).

<sup>2</sup> For notation see Brönsted, *ibid.*, 42, 761 (1920).

<sup>3</sup> Bjerrum, *Z. Elektrochem.*, 24, 321 (1918). Brönsted, Ref. 2.

<sup>4</sup> Lewis and Linhart, *THIS JOURNAL*, 41, 1955 (1919).

passing from one salt to another. It lacks, however, as does Equation 1, the property of a uniform convergence with decreasing concentration.

From the point of view of the complete dissociation of the strong electrolytes it was previously pointed out by the writer,<sup>5</sup> that the separate or individual behavior of ions may be accounted for by attributing to them a secondary power beside the primary *Milner* effect, and some possible reason for the appearance of such a secondary power was mentioned. The leading idea of the present paper assumes that the osmotic deviation is determined by two such separate influences, one of which—namely, the pure *Milner* effect—being the only one perceptible at small concentrations, while for the secondary effect laws similar to those governing non-electrolytes dissolved in salt solutions must be assumed. As will appear from the following discussion a very satisfactory expression of thermodynamic properties of salt solutions can be derived from this point of view.

## 2. The Osmotic Deviation: A General Formula

As a good many earlier investigations have shown, addition of salts to a solution of a non-electrolyte causes a change, mostly an increase, in the activity of the non-electrolyte. This effect known as the "salting-out effect" is generally directly proportional to the concentration of the salt added. The assumption of a similar influence of salts upon the activity of ions in spite of the very different total effect in the two cases appears reasonable, because the sequence in which the influence manifests itself is generally the same.<sup>6</sup>

On the ground of this view we must assume the osmotic deviation of a salt solution to be represented by an equation of the following form

$$1 - \varphi = f(c) + \beta c \quad (3)$$

where  $f(c)$  is a universal function and  $\beta$  a coefficient peculiar to the salt considered.

Inspection of the best measurements of osmotic and activity coefficients now shows Equation 3 to be satisfied for uni-univalent salts by introducing  $f(c) = \alpha\sqrt{c}$  where  $\alpha$  is a universal constant possessing at least approximately the value 0.32 at 0°. We can then write

$$1 - \varphi = \alpha\sqrt{c} + \beta c \quad (4)$$

as presumably of universal validity; and

$$1 - \varphi = 0.32\sqrt{c} + \beta c \quad (5)$$

as valid at 0° or in the neighborhood of this temperature.

<sup>5</sup> Ref. 2, p. 781.

<sup>6</sup> This rule has been verified in this laboratory using as non-electrolyte the substance trinitro-tri-amine cobalt, which according to Werner's theory is an undissociated compound. In this case the solubility is strongly increased by most salts, contrary to the usual salting-out effect. A marked parallelism between the influence upon the non-electrolyte and the isomeric salt, flavo cobaltic tetranitro-di-amine cobaltate by various salts was noted.

While the second term in these equations accounts for such effects as are peculiar to each solution, the square-root term represents the influence of the simple inter-ionic forces due to the electrical net charge. It is interesting to note that Milner's calculation of this electrical effect also leads to a square-root expression (even if the  $\alpha$ -values calculated in this way do not agree with that given here.<sup>7</sup>

Of the properties belonging to Equations 4 and 5 we may mention the fulfilment of the requirement referred to above, that as concentration decreases the same ideal curve for all electrolytes of the type considered is approached. This is due to the fact that as the concentration approaches zero the term  $\beta c$  accounting for the individuality of the solutions becomes infinitely small compared with the general term  $\alpha\sqrt{c}$ .<sup>8</sup>

The concentration at which this ideal form of our equation, namely,

$$1 - \varphi = \alpha\sqrt{c} \quad (6)$$

or

$$1 - \varphi = 0.32\sqrt{c} \quad (7)$$

is applicable depends upon the value of  $\beta$ . This coefficient, being usually of the same order of magnitude as  $\alpha$ , the simple form of our equation will usually become applicable from 0.01 or 0.001 *N* solution downwards.

The following sections contain the experimental basis of our Equations 4 to 7. In the first of them is given the most direct verification by means of freezing-point measurements. In the subsequent sections expressions for the activity coefficients and verification procured by means of electrometric and solubility measurements with and without the help of the principle of the specific interaction<sup>9</sup> of ions are developed.

### 3. Verification by Means of Freezing-point Measurements

Only very few measurements of freezing-point lowerings at 0.01 *N* and lower concentrations are sufficiently accurate to secure a reliable basis for a theory of salt solutions. The best existing freezing-point measurements are those of Adams<sup>10</sup> on potassium chloride and potassium nitrate and those of Harkins and Roberts<sup>11</sup> on sodium chloride. The osmotic coefficients  $\varphi$  calculated from these measurements at rounded concentrations are given in Table I.

<sup>7</sup> The results of Milner's calculations can be given in the form  $1 - \varphi = 0.25 c^{0.49}$ .

<sup>8</sup> In a recent paper by Lewis and Randall [THIS JOURNAL, 43, 1121 (1921)] it is suggested that  $n$  in the Lewis and Linhart expression (Equation 2) may equal  $1/2$  in the case of uni-univalent salts. If we make this assumption the expression of Lewis and Linhart conforms with the above Equation 6, but the individual properties of the substances are then not accounted for as in Equation 4 and the expression obtained, therefore, is valid only at high dilution.

<sup>9</sup> Brösted, THIS JOURNAL, 44, 877 (1921).

<sup>10</sup> Adams, *ibid.*, 37, 492 (1915).

<sup>11</sup> Harkins and Roberts, *ibid.*, 38, 2876 (1916). The figure at 0.0836 *N* has been omitted in the following treatment as evidently erroneous.

TABLE I

OSMOTIC COEFFICIENT  $\phi$  OF  $\text{KNO}_3$ ,  $\text{KCl}$  AND  $\text{NaCl}$  AT VARIOUS CONCENTRATIONS  
 $c(t=0^\circ)$ 

$c$	$\phi_{\text{KNO}_3}$	$\phi_{\text{KCl}}$	$\phi_{\text{NaCl}}$
0.005	0.976	0.980	0.982
0.01	0.968	0.971	0.973
0.02	0.954	0.961	0.958
0.05	0.923	0.943	0.945
0.1	0.889	0.927	0.934

The values of  $\beta$  computed from these data are  $+0.10$ ,  $-0.28$  and  $-0.35$  for  $\text{KNO}_3$ ,  $\text{KCl}$  and  $\text{NaCl}$ , respectively. Introducing these values in Equation 4 we obtain

$$\left. \begin{aligned} (1-\phi)_{\text{KNO}_3} &= 0.32\sqrt{c} + 0.10c \\ (1-\phi)_{\text{KCl}} &= 0.32\sqrt{c} - 0.28c \\ (1-\phi)_{\text{NaCl}} &= 0.32\sqrt{c} - 0.35c \end{aligned} \right\} \quad (8)$$

The osmotic deviations  $1-\phi$  calculated from these equations are given in Table II together with those calculated from the experimental  $\phi$ -values in Table I. In the last column the values of  $0.32\sqrt{c}$  are given.

TABLE II

OSMOTIC DEVIATIONS  $1-\phi$  FOUND (f) AND CALCULATED (c)

$c$	$\text{KNO}_3$		$\text{KCl}$		$\text{NaCl}$		$0.32\sqrt{c}$
	$(1-\phi)_f$	$(1-\phi)_c$	$(1-\phi)_f$	$(1-\phi)_c$	$(1-\phi)_f$	$(1-\phi)_c$	
0.005	0.024	0.023	0.020	0.021	0.018	0.020	0.022
0.01	0.032	0.033	0.029	0.029	0.027	0.028	0.032
0.02	0.046	0.047	0.039	0.040	0.042	0.038	0.045
0.05	0.077	0.077	0.057	0.058	0.055	0.054	0.072
0.1	0.111	0.111	0.073	0.073	0.066	0.066	0.101

The agreement between the values of  $1-\phi$  found and calculated leaves nothing to be desired. It is of particular interest that our equation holds equally in the case of positive and negative  $\beta$ -values, representing respectively negative and positive salting-out effects exerted by the salts on their own ions.

Other measurements of high value are those of Hall and Harkins<sup>12</sup> on potassium and sodium iodates. They agree approximately with the expression

$$(1-\phi) = 0.32\sqrt{c} + 0.17c$$

Slight deviations between the values found and calculated are compatible with the assumption of experimental errors of the order of magnitude  $0.0002^\circ$  in the freezing points of the most dilute solutions.

On turning to the application of our formula to other freezing-point measurements as a rule we no longer find such agreement as in the cases mentioned. This, however, is no serious objection to its validity, because most earlier investigations lack that high degree of precision necessary

<sup>12</sup> Hall and Harkins, *THIS JOURNAL*, 38, 2658 (1916).

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activity coefficients of all salts and ions to be uniformly dependent on concentration.

### Verification by Means of Electrical Measurements

Experimental material available for checking the equations setting up in this section is in the results of the electrometric measurements of Ellis<sup>14</sup> and Linhart<sup>15</sup> on cells of the type,  $H | HCl | Ag$ , with hydrochloric acid of various concentrations. By these measurements, the relative values of the activity coefficient of the hydrochloric acid are determined. The comparison is made by assuming the solutions of hydrochloric acid to be *ideal dilute* solutions, *i. e.*, attributing to them the values appearing in Equation 14.

The values obtained in this way are given in the second column of Table III. The third column contains the values of  $f$  calculated from Equation 14, and in the last column are given the ideal values from Equation 14.

TABLE III

ACTIVITY COEFFICIENTS OF HCl, FOUND AND CALCULATED

$c$	$f_{\text{found}}$	$f_{\text{calc.}}$	$f_{\text{ideal}}$
0.0001	...	0.991	0.991
0.0002	...	0.987	0.987
0.0005	0.978	0.979	0.979
0.001	0.971	0.971	0.970
0.002	0.958	0.959	0.958
0.005	0.934	0.938	0.934
0.01	0.912	0.915	0.908
0.02	0.882	0.886	0.873
0.05	0.848	0.850	0.824
0.1	0.803	0.784	0.737

The value inserted in Equation 11 for the calculation of  $f_{\text{calc.}}$  is the value of  $f$  obtained from the equation employed therefore:

$$\ln f = -0.96\sqrt{c} + 0.62c \quad (15)$$

The highest concentration 0.1 *N* is dispensed with the agreement between  $f_{\text{found}}$  and  $f_{\text{calc.}}$  is seen to be complete. Comparison with the values in the last column shows the hydrochloric acid solutions to be ideal up to 0.002 *N*.

The electrometric measurements, therefore, fully verify our theory. The value  $1 - \phi = 0.32\sqrt{c} - 0.31c$ , derivable from (15) is very similar to that obtained for potassium and sodium chlorides by using the same data and shows that hydrochloric acid at the dilutions here considered exhibits no peculiar behavior such as previous experiments on other acids might lead us to suspect.

ELLIS, THIS JOURNAL, 39, 2532 (1917).

LINHART, *ibid.*, 41, 1175 (1919).



to secure reliable results at the lower concentrations. This, for instance, is clearly demonstrated when the values collected by Noyes and Falk are introduced in the above calculations. We find in this case no agreement at all with our formula. Most previous experimental material in this field is therefore unserviceable for the establishment or verification of a theory of solution.

Fortunately the freezing-point method is not the only way of obtaining information about thermodynamic properties of solutions. For the use of other methods, however, it is necessary to develop the relationship between the osmotic deviation as dealt with in this section and the activity functions on the basis of our theory as given by Equation 4.

#### 4. Calculation of Activity Coefficients

When Equation 4 is connected with the general relation between osmotic and activity coefficients<sup>13</sup> the following equation results,

$$\ln f = -3\alpha\sqrt{c} - 2\beta c \quad (9)$$

where  $f$  stands for the activity coefficient of the salt. Corresponding equations hold for the activity coefficients  $f'$  and  $f''$  for the cation and anion, respectively, namely

$$\left. \begin{aligned} \ln f' &= -3\alpha\sqrt{c} - 2\beta'c \\ \ln f'' &= -3\alpha\sqrt{c} - 2\beta''c \end{aligned} \right\} \quad (10)$$

the three activity coefficients being correlated by  $f^2 = f'f''$ , and the  $\beta$ -coefficients, therefore, by  $2\beta = \beta' + \beta''$ .

Introducing into Equations 9 and 10 the value  $\alpha = 0.32$  found in the foregoing section, we obtain

$$\left. \begin{aligned} \ln f &= -0.96\sqrt{c} - 2\beta c \\ \ln f' &= -0.96\sqrt{c} - 2\beta'c \\ \ln f'' &= -0.96\sqrt{c} - 2\beta''c \end{aligned} \right\} \quad (11)$$

We see thus that the activity coefficients of salts are determined by two terms, one of which is universal, independent of the nature of the salt concerned, while the other accounts for its individual property. As the latter is directly proportional to the concentration we shall find the same to be true when comparing 2 different salts, as is clearly shown by the following simple equation.

$$\ln \frac{f_1}{f_2} = -2(\beta_1 - \beta_2)c \quad (12)$$

Equation 11 allows a direct calculation of activity coefficients from osmotic measurements, by which the value of the  $\beta$ -coefficient is furnished. At high dilution the equation assumes the simple form,

$$\ln f = \ln f' = \ln f'' = -3\alpha\sqrt{c} \quad (13)$$

and at 0°

$$\ln f = \ln f' = \ln f'' = -0.96\sqrt{c} \quad (14)$$

<sup>13</sup> Ref. 2, p. 765.

showing the activity coefficients of all salts and ions to be uniformly determined by the concentration.

### 5. Verification by Means of Electrical Measurements

The best experimental material available for checking the equations set up in the foregoing section is in the results of the electrometric measurements of Noyes and Ellis<sup>14</sup> and Linhart<sup>15</sup> on cells of the type,  $H | HCl | Ag-Cl.Ag$ , containing acid of various concentrations. By these measurements, however, only relative values of the activity coefficient of the hydrochloric acid are furnished. The comparison is made by assuming the solutions of lowest concentration to be *ideal dilute* solutions, *i. e.*, attributing to them the  $f$ -value appearing in Equation 14.

The values obtained in this way are given in the second column of Table III. The third column contains the values of  $f$  calculated from Equation 2, and in the last column are given the ideal values from Equation 14.

TABLE III  
ACTIVITY COEFFICIENTS OF HCl, FOUND AND CALCULATED

$c$	$f_{\text{found}}$	$f_{\text{calc.}}$	$f_{\text{ideal}}$
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0.001	0.971	0.971	0.970
0.002	0.958	0.959	0.958
0.005	0.934	0.938	0.934
0.01	0.912	0.915	0.908
0.02	0.882	0.886	0.873
0.05	0.848	0.850	0.824
0.1	0.803	0.784	0.737

The  $\beta$ -value inserted in Equation 11 for the calculation of  $f_{\text{calc.}}$  is  $-0.31$  and the equation employed therefore:

$$\ln f = -0.96\sqrt{c} + 0.62c \quad (15)$$

When the highest concentration  $0.1 N$  is dispensed with the agreement between  $f_{\text{found}}$  and  $f_{\text{calc.}}$  is seen to be complete. Comparison with the figures in the last column shows the hydrochloric acid solutions to be *ideal*, at least up to  $0.002 N$ .

These electrometric measurements, therefore, fully verify our theory. The equation,  $1-\phi=0.32\sqrt{c}-0.31c$ , derivable from (15) is very similar to Equation 8 obtained for potassium and sodium chlorides by using freezing-point data and shows that hydrochloric acid at the dilutions here considered exhibits no peculiar behavior such as previous experiments on this subject might lead us to suspect.

<sup>14</sup> Noyes and Ellis, *THIS JOURNAL*, 39, 2532 (1917).

<sup>15</sup> Linhart, *ibid.*, 41, 1175 (1919).

It is very remarkable that the value 0.32 of  $\alpha$  derived from freezing-point measurements applies here at the temperature of the experiment, 25°. The assumption of an approximate independence of the temperature of the  $\alpha$ -coefficient is, however, also corroborated by solubility measurements as referred to in the following sections.<sup>16</sup>

## 6. Verification by Means of Solubility Data

When a salt is dissolved in very small amount in a salt solution of the (total) concentration  $c$ , Equations 9 to 11 must hold for the dissolved salt,  $\beta$ ,  $\beta'$  and  $\beta''$  being constants which depend upon the nature of the dissolved salt as well as the salt solution serving as solvents. The theory is, therefore, directly applicable to the problem of calculating solubilities of slightly soluble salts in salt solutions of varying concentration.

**Solubility in the Ideal Region of Concentrations.**—In this region Equation 9 simplifies into

$$\ln f = -3\alpha\sqrt{c} \quad (13)$$

Since at constant temperature the solubility of a salt is inversely proportional to its activity coefficient, we can write

$$\ln s/s_0 = 3\alpha(\sqrt{c_0} - \sqrt{s_0}) \quad (16)$$

or by introduction of the value of  $\alpha$

$$\ln s/s_0 = 0.96(\sqrt{c_0} - \sqrt{s_0}) \quad (17)$$

In these equations  $s_0$  is the solubility in pure water,  $s$  in a hetero-ionic salt solution of very low concentration  $c$ , and  $c$ , the total concentration  $c+s$ .

Some few results obtained in this laboratory in order to verify Equation 17 are tabulated below. The sparingly soluble salts examined were as follows: (1) oxalo-cobaltic tetrathiocyanato-diammine chromiate,  $[\text{Co}(\text{NH}_3)_4\text{C}_2\text{O}_4] [\text{Cr}(\text{NH}_3)_2(\text{CNS})_4]$ ; (2) croceo-cobaltic tetranitro-diammine cobaltiate,  $[\text{Co}(\text{NH}_3)_4(\text{NO}_2)_2] [\text{Co}(\text{NH}_3)_2(\text{NO}_2)_4]$ ; (3) croceo-cobaltic tetrathiocyanato-diammine chromiate,  $[\text{Co}(\text{NH}_3)_4(\text{NO}_2)_2] [\text{Cr}(\text{NH}_3)_2(\text{CNS})_4]$ ;

TABLE IV

SOLUBILITY OF METAL AMMONIA SALTS IN VERY DILUTE SALT SOLUTIONS.  $t=20^\circ$

$c$	$c_t$	$(s/s_0)_{\text{found}}$	$(s/s_0)_{\text{calc.}}$
	1. Oxalo-chromiate. $s_0=0.00137$		
0.000	0.00137	1.000	1.000
0.001	0.00239	1.011	1.012
0.002	0.00340	1.023	1.021
	2. Croceo-cobaltiate. $s_0=0.000370$		
0.000	0.00037	1.000	1.000
0.001	0.00138	1.021	1.019
0.002	0.00238	1.035	1.029
	3. Croceo-chromiate. $s_0=0.000143$		
0.000	0.000143	1.000	1.000
0.001	0.00115	1.025	1.021

<sup>16</sup> Regarding the influence of changing temperature on activity coefficients, see Brönsted, *Z. physik. Chem.*, 100 (1922).

solutions of sodium chloride, potassium chloride and potassium nitrate were used as solvents. The highest concentration used being 0.002 *N*, no difference in solvent power of the three solvents could be observed, and so only the mean values are given in the table.

The agreement between the values of  $s/s_0$  found and calculated is satisfactory and proves that the square-root expression holds in the region of concentration 0.00014 *N* to 0.002 *N* used here.

Experiments are in progress in this laboratory to secure accurate solubility data at still lower concentrations.

**Solubility at Higher Concentrations.**—When, in the general equation for the solubility equilibrium in hetero-ionic solvent

$$s^2 f' f'' = s_0^2 f_0^2 \quad (18)$$

the  $f$ -values as given in Equations 9 and 10 are introduced, we obtain

$$\ln s/s_0 = 3\alpha(\sqrt{c_i} - \sqrt{s_0}) + \beta c \quad (19)$$

where  $\beta$  is a constant depending upon the ionic interaction and salting out effect of the solvent and  $\alpha$  has the usual value 0.32.

In the case of a homo-ionic solvent we have in the place of (18)

$$sc_i f' f'' = s_0^2 f^2, \quad (20)$$

and thus in the same way

$$\frac{1}{2} \ln \frac{sc_i}{s_0^2} = 3\alpha(\sqrt{c_i} - \sqrt{s_0}) + \beta c \quad (21)$$

A considerable amount of experimental material from a recently published investigation<sup>17</sup> on solubility of metal ammonia salts is available for checking these equations. A series of examples taken from this source has been recalculated with the aid of Equation 19 inserting  $3\alpha = 0.96$ , and for  $\beta$  that value which gives the closest agreement with the experimental results. The data concerned, valid at 0°, are given in Table V.

The agreement between the values of  $s/s_0$  found and calculated as exhibited by this table is in most cases very close, which is the more remarkable as the  $\beta$ -values introduced vary extraordinarily. Equation

TABLE V

SOLUBILITY RATIO  $s/s_0$  FOUND AND CALCULATED FOR METAL AMMONIA SALTS IN VARIOUS SOLVENTS

<i>c</i>	$(s/s_0)_{\text{found}}$	$(s/s_0)_{\text{calc.}}$
1. Praseo cobaltic iodate in potassium chloride, $s_0 = 0.00441$ , $\beta = +0.20$		
0.00	1.000	1.000
0.02	1.104	1.097
0.05	1.191	1.187
0.1	1.295	1.307

<sup>17</sup> Brönsted and Agnes Petersen, *THIS JOURNAL*, 43, 2265 (1921).

TABLE V (continued)

$c$	$(s/s_0)_{\text{found}}$	$(s/s_0)_{\text{calc.}}$
2. Praseo cobaltic bromide in potassium formate, * $s_0 = 0.00632$ , $\beta = -0.58$		
0.00	1.000	1.000
0.02	1.082	1.072
0.05	1.143	1.132
0.1	1.198	1.198
0.2	1.280	1.280
3. $\beta$ -Croceo cobaltic nitrate in potassium formate, $s_0 = 0.00494$ , $\beta = -0.16$		
0.00	1.000	1.000
0.02	1.086	1.085
0.05	1.164	1.162
0.1	1.258	1.258
0.2	1.404	1.403
4. Croceo cobaltic perchlorate in potassium formate, $s_0 = 0.0124$ , $\beta = +0.14$		
0.00	1.000	1.000
0.05	1.148	1.154
0.1	1.284	1.283
5. Croceo cobaltic dioxalo-tri-ammine cobaltiate in potassium chloride, $s_0 = 0.000593$ , $\beta = +0.78$		
0.00	1.000	1.000
0.02	1.186	1.158
0.05	1.332	1.311
0.1	1.546	1.546

\* The mean values of the data for potassium formate, tri-, di- and monochloro-acetate have been taken.

19 obviously applies much better than the cube-root expression used in the previous papers.

The results given here lend strong support to the applicability of the formulas applied for these calculations and therefore to the underlying theory as represented by the fundamental Equations 5 and 9.

### 7. Application of the Theory of the Specific Interaction of the Ions

When Equation 4 is applied to two salt solutions with a common ion, sodium chloride and potassium chloride, for instance, we can write

$$\begin{aligned}(1-\varphi)_{\text{NaCl}} &= \alpha\sqrt{c} + \beta_{\text{NaCl}}c \\ (1-\varphi)_{\text{KCl}} &= \alpha\sqrt{c} + \beta_{\text{KCl}}c\end{aligned}$$

and so

$$-(\varphi_{\text{NaCl}} - \varphi_{\text{KCl}}) = (\beta_{\text{NaCl}} - \beta_{\text{KCl}})c \quad (22)$$

Furthermore we have according to Equation 9

$$\begin{aligned}-\ln f_{\text{NaCl}} &= 3\alpha\sqrt{c} + 2\beta_{\text{NaCl}}c \\ -\ln f_{\text{KCl}} &= 3\alpha\sqrt{c} + 2\beta_{\text{KCl}}c\end{aligned}$$

and so

$$-\frac{1}{2} \ln \frac{f_{\text{NaCl}}}{f_{\text{KCl}}} = (\beta_{\text{NaCl}} - \beta_{\text{KCl}})c. \quad (23)$$

Combining Equations 22 and 23 we obtain,

$$\varphi_{\text{NaCl}} - \varphi_{\text{KCl}} = \frac{1}{2} \ln \frac{f_{\text{NaCl}}}{f_{\text{KCl}}} \quad (24)$$

In a recent paper<sup>9</sup> the writer has shown, on the basis of the principle of the specific interaction of the ions, the following equation to hold.

$$\varphi_{\text{NaCl}} - \varphi_{\text{KCl}} = \frac{1}{2} \ln \frac{f_{\text{Cl}}(\text{NaCl}) f(\text{Na})}{f_{\text{Cl}}(\text{KCl}) f(\text{K})} \quad (25)$$

where  $f_{\text{Cl}}(\text{NaCl})$  and  $f_{\text{Cl}}(\text{KCl})$  denote the activity coefficients of the chlorine ion in NaCl and KCl solutions respectively, and  $f(\text{Na})$  and  $f(\text{K})$  what are called the salting-out coefficients. Now combining Equations 24 and 25 the following relation results,

$$\frac{f_{\text{NaCl}}}{f_{\text{KCl}}} = \frac{f_{\text{Cl}}(\text{NaCl}) f(\text{Na})}{f_{\text{Cl}}(\text{KCl}) f(\text{K})} \quad (26)$$

Bearing in mind that  $f^2 = f'f''$  or  $f_{\text{NaCl}}^2 = f_{\text{Na}}(\text{NaCl}) f_{\text{Cl}}(\text{NaCl})$  and that  $f_{\text{Na}}(\text{NaCl}) = f_{\text{Na}}(\text{Cl}) f(\text{Na}) f(\text{Cl})$  etc.,  $f_{\text{Na}}(\text{Cl})$  indicating the coefficient of interaction of the sodium ion in a chloride solution, Equation 26 may be rewritten as follows.

$$\frac{f_{\text{Na}}(\text{NaCl}) f_{\text{Cl}}(\text{NaCl})}{f_{\text{K}}(\text{KCl}) f_{\text{Cl}}(\text{KCl})} = \left( \frac{f_{\text{Cl}}(\text{NaCl}) f(\text{Na})}{f_{\text{Cl}}(\text{KCl}) f(\text{K})} \right)^2$$

or

$$\frac{f_{\text{Na}}(\text{NaCl})}{f_{\text{K}}(\text{KCl})} = \frac{f_{\text{Cl}}(\text{NaCl})}{f_{\text{Cl}}(\text{KCl})} \left( \frac{f(\text{Na})}{f(\text{K})} \right)^2 \quad (27)$$

or

$$\frac{f_{\text{Na}}(\text{Cl})}{f_{\text{K}}(\text{Cl})} = \frac{f_{\text{Cl}}(\text{Na})}{f_{\text{Cl}}(\text{K})} \left( \frac{f(\text{Na})}{f(\text{K})} \right)^2 \quad (28)$$

Since the right-hand side of Equations 27 and 28, as shown in the paper quoted is determinable from solubility measurements we are in a position by means of these two equations to calculate the ratio of the activity coefficients and the ratio of interaction of the potassium and sodium ions or generally of two different ions with the same sign.

In the case of the alkali chlorides and nitrates we have found in the previous paper at 0°

$$\frac{f(\text{Na})}{f(\text{K})} = 1.010, \quad \frac{f_{\text{Cl}}(\text{Na})}{f_{\text{Cl}}(\text{K})} = 1.000, \quad \frac{f_{\text{NO}_3}(\text{Na})}{f_{\text{NO}_3}(\text{K})} = 1.028$$

and are so able to calculate the activity ratios of the alkali ions as follows.

$$\begin{aligned} \frac{f_{\text{Na}}(\text{Cl})}{f_{\text{K}}(\text{Cl})} &= 1.000 \cdot 1.010^2 = 1.020 \\ \frac{f_{\text{Na}}(\text{NaCl})}{f_{\text{K}}(\text{KCl})} &= 1.010 \cdot 1.010^2 = 1.030 \\ \frac{f_{\text{Na}}(\text{NO}_3)}{f_{\text{K}}(\text{NO}_3)} &= 1.028 \cdot 1.010^2 = 1.049 \\ \frac{f_{\text{Na}}(\text{NaNO}_3)}{f_{\text{K}}(\text{KNO}_3)} &= 1.038 \cdot 1.010^2 = 1.059 \end{aligned}$$

In the question of activity coefficients the theory here presented leads clearly a step further than the mere application of the principle of the specific interaction. Equation 28 obviously shows that the coefficients of interaction and the salting-out coefficients are correlated by an equation into which the nature of the common ion does not enter. In case an additional inquiry into this matter should prove Equation 28 to be generally valid, it would certainly contribute to the solution of the question of the mechanism of bringing about an effect of electrical interaction between ions, such as was shown in the paper referred to as necessary in order to be able to account for the peculiarities of salt solutions.

### Summary

From the point of view that the individualities of salt solutions have an origin similar to that of the individual salting-out effect in the case of non-electrolytes, equations were set up to govern the osmotic and activity functions of uni-univalent salts in pure and mixed solutions.

These equations were found to be strongly supported by the most accurate experimental results including measurements of freezing-point lowerings, electromotive force and solubilities.

Ratios of activity coefficients were calculated on the ground of these equations in conjunction with the principle of the specific interaction of ions.

COPENHAGEN, DENMARK

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[CONTRIBUTION FROM THE RESEARCH LABORATORY OF THE NATIONAL BISCUIT COMPANY, No. 7]

## THE USE OF PHTHALATE SOLUTIONS FOR HYDROGEN ELECTRODE STANDARDS

BY EARLE T. OAKES AND HENRY M. SALISBURY

Received August 5, 1921

The recent proposals to replace the calomel electrode by phthalate solutions as standard hydrogen electrodes led the present authors to investigate the reliability of such solutions.

A buffer solution of potassium hydrogen phthalate and sodium hydroxide was made up as described by Clark and Lubs.<sup>1</sup> Fifty cc. of 0.2 *M* potassium hydrogen phthalate solution and 45.45 cc. of 0.2 *M* sodium hydroxide were mixed and diluted to 200 cc. with conductivity water. This solution was made up to give a Sørensen value of 6.0 and when tested by indicators this value was obtained.

Using the method described by Beans and Oakes<sup>2</sup> a quantity of this solution was tested by the hydrogen electrode. Measurements were taken

<sup>1</sup> Clark and Lubs, *J. Biol. Chem.*, **35**, 3, 504 (1916).

<sup>2</sup> Beans and Oakes, *THIS JOURNAL*, **42**, 2116 (1920).

over a period of 48 hours. During this time there was a continued increase in the observed e.m.f. as shown in Curve 1, Fig. 1. At the end of 48.5 hours the solution, whose original Sørensen value was 6.0 had a Sørensen value of 7.01. A portion of the solution removed from the electrode chamber at the end of 48.5 hours gave a Sørensen value of 7.0 by indicators.

A second solution of approximately 0.2 *M* potassium hydrogen phthalate was freshly made up with conductivity water and when tested with indicators was found to have a Sørensen value of 3.9. A portion of this solution in the hydrogen electrode chamber gave the results plotted in Curve 3, Fig. 1. Here again the phthalate buffer solution continued to

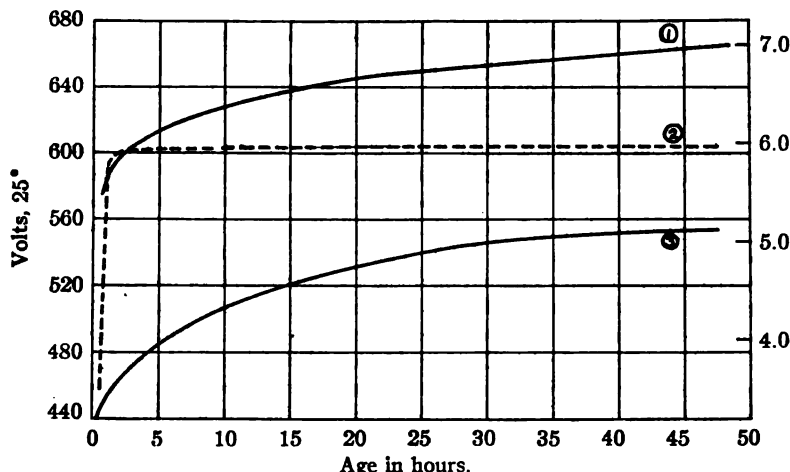


Fig. 1.—Observed e. m. f. change with the time. (1) Potassium hydrogen phthalate and sodium hydroxide. (2) Monopotassium phosphate and sodium hydroxide. (3) Potassium hydrogen phthalate.

increase steadily in voltage during the entire course of the experiment.

As a control on the equipment, method and manipulation, a solution consisting of 50 cc. of 0.2 *M* monopotassium phosphate and 8.70 cc. of 0.2 *M* sodium hydroxide diluted to 200 cc. with conductivity water was investigated. This solution was made up to give a Sørensen value of 6.0 and when tested by indicators was found to have a Sørensen value of 6.0.

Since this solution came to a constant voltage after 8 hours the actual values obtained are given in Table I and plotted in Curve 2, Fig. 1.

Time		$P_H$	Time		$P_H$
Hrs.	Min.		Hrs.	Min.	
	30	3.52	7	48	5.96
	42	4.96	30	20	5.96
1	7	5.80	47	30	5.96
4	58	5.91			



In these determinations the chain  $\text{Hg}|\text{HgCl}, \text{KCl}(\text{Sat})|\text{KCl}(\text{Sat})| \text{Buffer}$   
 Solution  $|\text{H}_2$  was used in which  $e_2 = e_1$  - observed e.m.f.  $e_1 = 0.5266$   
 volts.<sup>3</sup> The Sørensen values were calculated according to the formula  
 $P_{\text{H}} = \frac{-E_2}{0.05916} - \log K$ . Assuming  $\alpha$  0.1 M HCl at  $25^\circ = 0.92 K$ , the  
 equilibrium constant of  $2\text{H}^+ \rightleftharpoons \text{H}_2 = 10^{-4.671}$  at  $25^\circ$ .

As a further check on these results, a different sample of pure phthalic anhydride was secured and solutions of the acid phthalate were tested in the manner described above with practically the same results. There was a continuous drift throughout the 48 hours of observation, the Sørensen value of the buffer increasing continuously.

The hydrogen gas was purified by passing it first through alkaline permanganate solution, through alkaline pyrogallate solution, through a cotton plug and finally saturating with water vapor at  $25^\circ$ . The entire cell chain was placed in a water thermostat at  $25^\circ \pm 0.02^\circ$ .

In preparing our solution of potassium hydrogen phthalate the phthalic acid was first carefully sublimed, then the potassium acid phthalate purified by three recrystallizations. Hendrixson,<sup>4</sup> has shown that no increase in purification is effected by more than three recrystallizations. In recrystallizing, care was taken not to allow the temperature of the solution to fall below  $20^\circ$ .<sup>5</sup> The crystals were finally dried to constant weight at  $110$ – $115^\circ$ . Upon examination under the microscope all these crystals of acid phthalate were seen to be hexagonal plates with no needle forms present.

Conductivity water was used throughout this work. The hydrogen electrodes were of plate form freshly coated with platinum black and thoroughly cleaned. No corrections were made for changes in barometric pressure, as these corrections were too slight to affect the hydrogen-ion concentrations to an appreciable extent.

It is evident, then, that our most careful purification of these phthalate solutions failed to produce a product that gives a constant Sørensen value with the hydrogen electrode.<sup>6</sup> That the difficulties encountered are most certainly due to changes in the phthalate solutions and not to the apparatus or manipulation, is shown by the constancy of the results obtained with the same equipment on phosphate solutions and the fact that indicators recorded the same differences as did the hydrogen electrode. Furthermore, the drift is too great to be accounted for by a reduction of any impurity which could be present in only the most minute quantity if at all.

<sup>3</sup> Ostwald, *Z. physik. Chem.*, **35**, 333 (1900). Fales and Vosburgh, *THIS JOURNAL*, **40**, 1300 (1918). Fales and Mudge, *ibid.*, **42**, 2434 (1920).

<sup>4</sup> Hendrixson, *THIS JOURNAL*, **42**, 724 (1920).

<sup>5</sup> Dodge, *ibid.*, **42**, 1655 (1920).

<sup>6</sup> Since finishing this investigation A. R. T. Merrill, *ibid.*, **43**, 2688 (1921) in her work on cystine makes the statement: "The acetic acid-sodium acetate mixtures of Walpole were used in place of the potassium hydrogen phthalate solutions recommended by Clark and Lubs as the latter gave a decided drift when determining the hydrogen-ion concentration by the electrometric method, due possibly to reduction occurring." We have had three private communications from other workers who have experienced similar difficulty with phthalate solutions.

There is, of course, a slight possibility that even a minute trace of impurity might catalyze the reduction of the phthalate. Even if this is the case, it is clear that the most careful methods of purification fail to remove this catalyst and the use of phthalates for hydrogen electrode measurements would be justified only after carefully testing them for freedom from change under continued use.

The authors are indebted to Dr. F. D. Dodge for his kindness in testing the purity of our potassium hydrogen phthalate. Dr. Dodge reported that after carefully examining the products we had purified for both the initial and check experiments, he could detect no impurities and the two samples were identical in being pure potassium hydrogen phthalate.

### Summary

1. The most carefully purified phthalate solutions gave a progressive decrease in hydrogen-ion concentration when in continued contact with the hydrogen electrode.

2. This decrease in hydrogen-ion concentration is due to changes in the phthalate itself, probably a reduction reaction.

3. If impurities are responsible for the changes noted, their action must be that of catalysts in the reduction of the phthalate, as they could not possibly be present in sufficient quantity to account for the entire change by themselves.

NEW YORK, N. Y.

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[CONTRIBUTION FROM THE NELA RESEARCH LABORATORIES]

## RHYTHMIC DEPOSITION OF PRECIPITATED VAPORS

BY ENOCH KARRER

Received August 20, 1921

The phenomenon of rhythmic or periodic precipitation and allied phenomena has received considerable attention since Liesegang<sup>1</sup> recorded his observations of it, now referred to frequently as Liesegang's rings or phenomenon. A common illustration of this is the rhythmic precipitation of silver chromate in concentric rings, when a crystal of silver nitrate is placed upon a gelatin film containing some dichromate. The phenomenon may be of importance in geology and is of great importance in biology,<sup>2</sup> where striae so frequently encountered, may be recalled. For example the structure causing iridescence in mother-of-pearl<sup>3</sup> may be referable to this phenomenon as well as that in various insects and beetles

<sup>1</sup> Liesegang, "Chemischer Vorgänge in Gallerten," Leipzig, 1898.

<sup>2</sup> Liesegang, *Naturw. Wochenschr.*, 41 (1910). Bechhold, "Die Kolloide in Biologie und Medizin," Steinkopff, Leipzig, 1920.

<sup>3</sup> Pfund [*J. Franklin Inst.*, 183, 453 (1917)] has recently made a study of the color and structure of mother-of-pearl, concluding that no simple periodic condition of environment can account for it. For further illustration see Bechhold, Ref. 2.

and elsewhere. In the first case calcium carbonate has been periodically precipitated in *Conchliolin*. The structure of the retinal cones has been thus explained and it may also be suggested that the structure of the lens of the eye may be due to this process.

It appears that no adequate theory for this rhythmic precipitation has been presented.

Allied to rhythmic precipitation is the rhythmic stratification of sediment. This has received some attention from several authors, but most recently from Mendenhall and Mason.<sup>4</sup> These authors have shown that in the formation of layers of sediment suspended in water a temperature gradient laterally is essential. The distance between layers depends upon this gradient. They have shown that any two consecutive layers are on the confines of a system of convection currents in the liquid caused by the temperature gradient.

One might expect that the phenomenon would also take place in any two intermixing fluids, or solids, or liquid and fluid, just as in the present instance. Attempts by the author to produce such effects in water-vapor or steam and air in 1916 failed. It was thought that this case might be of interest in the formation of rhythmic or waves of clouds.<sup>5</sup> Experiments were then also made by using vapor such as of ammonia and hydrochloric acid which would enable one to see clearly the process of diffusion.

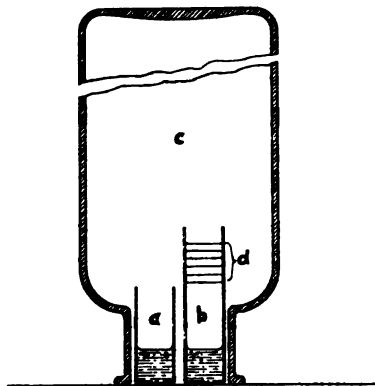


Fig. 1.

I wish now to describe the results of a few experiments which show that under suitable conditions a similar periodic formation will take place quite readily in vapors. The vapors whose behavior in this respect were first accidentally noticed are those of hydrochloric acid and ammonia.<sup>6</sup> If small vials (a,b) containing ammonia water and hydrochloric acid respectively are placed in an enclosure C as shown in Fig. 1 there will ensue diffusion of the vapors throughout the enclosure. During the diffusion of the vapor of one vial into the other vial the resulting pre-

cipitate will be deposited in a rhythmic manner upon the inner walls of

<sup>4</sup> Mendenhall and Mason, paper read before the annual meeting of the American Academy of Arts and Sciences, 1921.

<sup>5</sup> The common explanation of these is that due to Helmholtz stating that the precipitation is caused by low temperature of an adjacent region into which the water vapor is carried by ripples in the air.

<sup>6</sup> These vapors, among the best to make the course of convection currents apparent, were used to bring out the dark space around a hot wire. [See *J. Franklin Inst.*, 192, 737 (1921).]

one of the vials as is also indicated in Fig. 1, d. The deposition invariably takes place on the walls of the vial containing the hydrochloric acid. In all cases where I have observed this formation there has been a lateral temperature gradient of rather marked degree, and it appears that this is essential to the process just as Mendenhall and Mason have observed in case of solids suspended in liquids.

The distance between the rings of precipitate depends upon the temperature gradient, and seemingly upon the time interval between the beginning of the diffusion of the vapors into each other and the setting in of the temperature gradient. When the vials are left undisturbed and the external thermal conditions are changed the deposits also change. The rings of the precipitated salt are sharply defined and lie parallel to the surface of the liquid. Under the conditions where the rings were

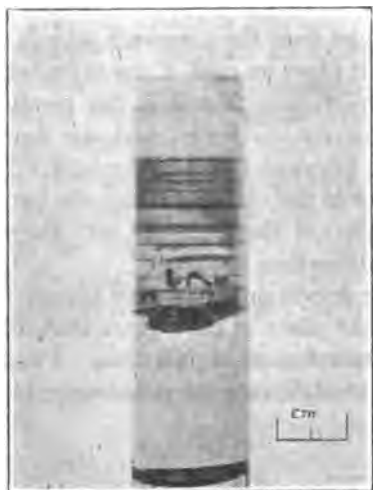


Fig. 2.



Fig. 3.

first observed, namely, after an intense beam of light had been passing through the enclosure, there were 6 or 8 rings to the centimeter. On other occasions there were more or less than this, the interval ranging from more than a centimeter to a fraction of a millimeter. In one instance the rings were so numerous that they could only with difficulty be distinguished by the unaided eye. In the latter case they formed overnight in vials which had been standing in the window exposed to intense heat of the sun.

The distance between the successive rings is seldom constant (Fig. 1), but increases or decreases gradually from the lowest upward; or, several such systems may appear. Reference has been made to the deposit only as rings upon the inner walls of the vial. These rings have, however, more or

less extension radially, and in fact may be complete disks, seen edgewise. In the latter case the rings mark, as it were, cellular partitions in the tube. The uppermost ring in one experiment (Fig. 3) shows such a partitioning film, which instead of remaining horizontal, had become conical after extending beyond the edge of the vial. The convection currents near the mouth of the vial were not horizontal. Within the vial each cell marks the boundaries of a system of vertical and horizontal convection currents, the necessary elements for the formation of which are a lateral temperature gradient and a vertical density gradient.

When these conditions are changed, even after a definite system of rings has formed, the rings will be readjusted, disappearing from the original location to reappear elsewhere; and, after several hours, a new system may have succeeded the old. It required from 6 to 8 hours for a complete system to form, but it is at times noticeable very much sooner than this.

The question may be asked: What part does the ammonia play in the stratification? It is very probable that it plays no part, if the explanation above given of the stratification is correct, *viz.*, that it is the resultant of two density gradients one due to gravity vertically, and one due to temperature laterally, together with the buoyant forces in the fluid. The stratification may then be already present in the vial containing the hydrochloric acid vapors and air. The diffusion of the ammonia into the vial is merely a means of making this stratification apparent.<sup>7</sup>

It would seem that, given the proper conditions, one may expect this same phenomenon of stratification to take place in pure gases that differ in density. Such cases may have meteorological significance. Finally, it may be of interest, too, to note that stratification in gas storage tanks is well known to gas engineers.

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[CONTRIBUTION FROM THE LABORATORY OF PHYSICAL CHEMISTRY OF ODESSA UNIVERSITY]

## NEGATIVE VISCOSITY

BY ADOLPH I. RABINOVICH

Received August 25, 1921

The phenomenon which has received the wrong name of "negative viscosity" consists in the tendency of certain salts to lessen the viscosity of water, when dissolved in it. If we take the viscosity of water as unity, the viscosity of these solutions will be less than unity, in some cases by 24%, but of course not truly negative.

In non-aqueous solutions the phenomenon of negative viscosity oc-

<sup>7</sup> (Note added March 1, 1922.) It appears that Dr. W. H. Chapin of Oberlin College, in using ammonium chloride and hydrochloric acid vapors to illustrate the laws of diffusion, had also observed and, I am told, exhibited this phenomenon in 1917.

curs very seldom. It has been observed so far only in glycerol for potassium iodide,<sup>1</sup> ammonium iodide, and rubidium chloride, bromide, nitrate and iodide,<sup>2</sup> and for naphthalene in alcohols.<sup>3</sup>

Many attempts at theoretical explanation have been made but none of them seems to be quite satisfactory. Lack of space prevents submitting them to critical examination, and therefore only the different factors acting upon the viscosity of solutions and especially those factors which are able to lower the internal friction of the solvent will be considered here.

1. One of the important factors which determine the viscosity of solutions is, obviously, the initial *viscosity of the solvent*. However, as this paper discusses only the relative viscosity of solutions (taking the internal friction of the solvent as unity), this factor will not be further considered.

2. The *viscosity of the solute* or the internal friction of the solution is not strictly an additive function of the coefficients of the components. All attempts to calculate accurately the viscosities of liquid mixtures on this basis have proved unsuccessful,<sup>4</sup> but the certain influence of the viscosity of the solute on the internal friction of the solution is undeniable. In aqueous solutions of salts it manifests itself in the high internal friction of very concentrated solutions, even of those salts which, at smaller concentrations, lower the viscosity of water.

When the viscosities of very strong solutions of different salts are compared, the dependence of viscosity in solutions upon the viscosities of the respective salts in the fused state becomes clear.

TABLE I  
VISCOSITIES OF CONCENTRATED SOLUTIONS AND FUSED SALTS

Salt	$\eta$ of fused salt at $t$ Cg. °C.	$\eta$ of 11.5 <i>N</i> sol. at 25° Cg.	$\eta_{\text{rel}}$ at 25°
NH <sub>4</sub> NO <sub>3</sub>	2.477	0.0452	2.5
	1.980		
	0.9 extrap. to 262		
ZnCl <sub>2</sub>	50.9	0.2769	153
	34.7 301		

The data for fused salts are taken from the work of Fousseureau<sup>5</sup> for solutions, but the calculations are mine. The figure for ammonium nitrate at 262 is extrapolated, using the known temperature coefficient of viscosity. The enormous difference in the internal friction of equiva-

<sup>1</sup> Getman, *THIS JOURNAL*, 30, 1077 (1908).

<sup>2</sup> Jones and Davis, *Carnegie Inst. Pub.*, 180, 191 *et seq.* (1913).

<sup>3</sup> W. Ostwald, "Grundriss der Kolloidchem." 2nd ed., p. 180.

<sup>4</sup> For bibliography see the paper of Faust, *Z. physik. Chem.*, 79, 97 (1912).

<sup>5</sup>  $\eta_{\text{rel}}$  is the relative viscosity of solution compared with the viscosity of water at the same temperature taken as unity.

<sup>6</sup> Fousseureau, *Ann. chim. phys.*, [6] 5, 241 (1885).

lent solutions at 25° corresponds closely to the similar difference in fused salts, at 262°.

3. *Hydration* increases the viscosity of solutions. For most of them  $\eta_r$  (the relative viscosity) rises with rising temperature. Only those which contain highly hydrated salts (of lithium, calcium and magnesium) diminish their relative viscosities when heated, owing to the thermal decomposition of hydrates. Furthermore, when a comparison of salts with a common anion is made it is seen that the highly hydrated cations increase to a large degree the viscosity of water in a normal solution, while the least hydrated diminish it.

TABLE II  
HYDRATION NUMBERS OF CATIONS

Chlorides	$\eta_r$ of <i>N</i> sol.	Hydration number <sup>7</sup>
Cs	0.9775	very small
Rb	0.9846	small
K	0.9872	22
NH <sub>4</sub>	0.9884 <sup>8</sup>	...
Na	1.0973 <sup>9</sup>	70
Li	1.1423	158

Jones<sup>10</sup> has interpreted this series in the directly opposite manner, taking into account only the atomic volumes of ions, without their hydrate envelopes. With regard to the mechanism of the increase in viscosity by hydration, it will be sufficient to call attention to the increase of the real concentration of the solution, *i. e.*, the diminution in the amount of free solvent, because a part is required for the formation of solvates (namely, hydrates) with the solute.

4. The *formation of complex ions and molecules* increases the viscosity when the volume of the complex ions is larger than the sum of the volumes of the simple ions composing it, and decreases the viscosity in the opposite case. Experimental evidence for these volume changes could be obtained from the change of relative viscosity with temperature, if the influence of temperature on the degree of complexity of some ions could be learned. Unfortunately, the only available data, those of Gordon<sup>11</sup> for cadmium salts, do not make it possible to solve this problem. In this connection, my own observation may present a certain interest, namely, that strong solutions of cadmium bromide show a decrease in relative viscosity, when the temperature is raised from 25° to 50°.

5. The *electric fields* of the ions may also affect the viscosity of solutions but cannot possibly diminish it, as Euler<sup>12</sup> supposed. The immedi-

<sup>7</sup> According to Riesenfeld and Reinhold, *Z. physik. Chem.*, 66, 672 (1909).

<sup>8</sup> Kanitz, *ibid.*, 22, 336 (1897).

<sup>9</sup> Reyher, *ibid.*, 2, 744 (1888).

<sup>10</sup> Jones, *Carnegie Inst. Pub.*, 80, p. 213; *Am. Chem. J.*, 37, 405 (1907).

<sup>11</sup> Gordon, *Z. physik. Chem.*, 23, 469 (1897).

<sup>12</sup> Euler, *ibid.*, 25, 536 (1898).

ate influence of the ionic electric fields upon the internal friction of the liquid should result in an increase in viscosity owing to the attraction between the electric charges on ions and the induced charges of opposite sign on the neighboring particles of the liquid, as has been shown by Sutherland.<sup>13</sup> Perhaps these attractions are manifested only in the formation, around the ions, of more or less stable envelopes of solvent particles, *i. e.*, in solvation or hydration.

6. A very important factor in the viscosity of solutions is *depolymerization*<sup>14</sup> of the associated solvent, especially of water, by dissolved substances. The theory of depolymerization may be stated thus: some liquids, such as water, glycerol, the alcohols, the organic acids, etc., contain associated or polymerized molecules which may dissociate into simple ones under the influence of temperature or pressure increase or upon the introduction of dissolved substances. It is generally accepted that such association exists. We do not possess as yet an accurate method of determining the composition and the relative amounts of different polymers composing an associated liquid, but many formulas enable us to find approximately the mean factor of association.<sup>15</sup> The same formulas which give inconsistent absolute values for this factor at a given temperature show concordant values for its decrease with rising temperature.

Change of pressure increases or decreases the factor of association of liquids in proportion to the relative size of the polymer and sum of the simple particles of a given liquid. In the case of water the relative sizes of particles of both kinds may be obtained by comparing the specific volume of liquid water with that of ice which is composed of more complex molecules. This has frequently been done.<sup>16</sup> Ice has the smaller density and the larger molecular volume; *i. e.*, the polymerization of water is accompanied by dilatation. This is indicated by the increase of the coefficient of thermal dilatation of water with heating. At lower temperatures the normal thermal dilatation is counterbalanced by the volume contraction caused by depolymerization. The effect of contraction can even exceed that of dilatation. This is the case below 4°. At higher temperatures depolymerization decreases, owing to diminution in the number of associated particles, and the coefficient of dilatation approximates its normal value.

Thus, every polymerized molecule of water has a larger volume than the sum of the volumes of simple particles composing it. If we represent the process of depolymerization of water,  $(\text{H}_2\text{O})_n \rightleftharpoons n(\text{H}_2\text{O})$ , as an ordi-

<sup>13</sup> Sutherland, *Phil. Mag.*, [6] 14, 1 (1907).

<sup>14</sup> The dissociation of molecular aggregates into simple particles.

<sup>15</sup> See the paper by D. Tyrer, *Z. physik. Chem.*, 80, 50 (1912), and later papers by the same author in different journals.

<sup>16</sup> Witt, *Kg. Wetensk. Akad. Förh.*, 1900, 68. Sutherland, *Phil. Mag.*, [5] 50, 460 (1900). Hudson, *Phys. Rev.*, 21, 16 (1905). Duclaux, *J. chim. phys.*, 10, 73 (1912).



nary process of dissociation (let us assume it to be isothermal), we can apply to it the well-known equation of Planck<sup>17</sup>

$$\frac{\partial(\ln K)}{\partial p} = - \frac{\Delta v}{RT}$$

from which it follows that if dissociation runs as it does here, under the volume contraction ( $\Delta v < 0$ ), the constant  $K$  and the degree of dissociation increase with rising external pressure  $p$ .

The same conclusion can be reached by applying the principle of Le Chatelier-Braun in the improved form given to it by Ehrenfest.<sup>18</sup>

The depolymerization effect of dissolved substances can be deduced from the effect of temperature and pressure by means of a rule enunciated by Tammann:<sup>19</sup> the introduction of soluble substances changes many properties of water such as its thermal dilatation, the temperature of maximum density, the compressibility, the specific heat, etc., in the same manner as does external pressure. Tammann explains this by the appearance of a real force, which he calls "internal pressure" (Binnendruck), and which is, in its action, analogous to external pressure.

The existence of such a force is quite probable, but Tammann overestimated its importance when he believed it to be the only one existing between the solvent and solute. This is shown by the discrepancy observed between the values of internal pressure when calculated by two different methods, amounting to 20–26% (in both directions) and even to 85% in one case. Moreover, solution of the alcohols in water lowers its internal pressure instead of increasing it, as would be expected if Tammann's effect were really the measure of attraction between the components of the solution.

The relations described by Tammann can be better explained by the theory of depolymerization, since the latter gives a simple and clear picture of the process, whereas Tammann's explanation is a purely formal description. Some facts (like the above-mentioned lowering of the internal pressure of water by alcohols), which are in contradiction to Tammann's view, can be readily accounted for on the basis of the theory of depolymerization. Thus, this theory is in perfect accord with the fact that a given solute has greater effect in raising the internal pressure the greater the association of the solvent (water > alcohol > ether > carbon disulfide).

Certain experimental data also strongly support this theory, such as cryoscopic determinations made on highly concentrated solutions, where water can be considered as the solute. Thus it has been shown by Jones

<sup>17</sup> M. Planck, "Thermodynamik," 4th ed., 1913, p. 235.

<sup>18</sup> Ehrenfest, *Z. physik. Chem.*, **77**, 227 (1911).

<sup>19</sup> Tammann, "Ueber die Beziehungen zwischen den inneren Kräften und Eigenschaften der Lösungen," 1907.

and Murrey<sup>20</sup> that when the molar concentration of water in acetic acid changes from 12.65 to 0.64, its molecular weight falls from 38.8 to 21.7. In formic acid water has the molecular weight 21.9 in a 6.18 *N* solution, and 19.7 in a 0.93 *N* solution.

Rozsa<sup>21</sup> has shown that the degree of association of water falls in acetic acid from 1.80 to 1.03 when the concentration changes from 15.13 to 0.213%, while in phenol it changes from 1.80 to 1.02 when the concentration diminishes from 16.10 to 0.406%.

It should be possible to make indirect cryoscopic determinations with inorganic salts as a solvent and small amounts of water as solute, thus measuring the solubility of salts at high temperatures. The depression of the melting point would correspond then to the freezing-point depression. For most salts these determinations would have to be made under pressure to prevent the evaporation of water at the high temperatures approximating the melting point of the salt. Such is the curve for silver nitrate drawn by Etard<sup>22</sup> for temperatures of 198°.

Unfortunately, these and similar measurements cannot be used to prove the depolymerizing influence of the change of concentration, as a quite analogous action is produced by pressure increase.

Far better results could be obtained with the double salt silver thallium nitrate, which is miscible with water in all proportions and melts at 82.5°. The quantity of this salt at my disposal was not great enough to allow cryoscopic determinations to be made.

Duclaux<sup>23</sup> indicated the depolymerization of water by dissolved substances, using a colorimetric method. He showed that the change of color of water to greenish was the same whether he raised its temperature or dissolved in it various salts. As the first influence is known to cause depolymerization, the author concluded that this is also the case with the second.

Of the possible causes of depolymerization of water, the effect of the volume of the dissolved substance may be mentioned first, as it is always acting, independently of the kind of solute. The concentration of the solvent is always diminished by the presence of the solute. If we suppose the mass-action law to be at least qualitatively applicable to the equilibrium between simple and polymeric molecules, the decrease in concentration must favor the decomposition of aggregates, *i. e.*, depolymerization. If  $V_1$  is the molecular volume of the solute,  $V_0$  that of the solvent,  $V$  that of the solution, then  $V_0 < V < V_0 + V_1$ . The influence is evidently the greater, the larger  $V_1$  and the smaller the contraction upon solution, that is  $(V_0 + V_1) - V$ . Such is the case with cane sugar,

<sup>20</sup> Jones and Murrey, *Am. Chem. J.*, **30**, 193 (1903).

<sup>21</sup> Rozsa, *Z. Elektrochem.*, **17**, 934 (1911).

<sup>22</sup> Etard, *Compt. rend.*, **108**, 176 (1889).

<sup>23</sup> Duclaux and Wollman, *J. Physik*, [5] **2**, 263 (1912).

which causes strong depolymerization of water, as far as we can judge of it by the lowering of the temperature of maximum density.

The second possible cause of depolymerization is the effect of the hydration of the solute in taking away a part of the solvent which is connected to the solute particles and lessening, therefore, the solvent concentration. Its necessary consequence, according to the mass-action law, is the displacement of equilibrium towards simple molecules. This factor has been considered by Traube,<sup>24</sup> Blanchard<sup>25</sup> and Bousfield.<sup>26</sup>

Third, a series of investigations has indicated that the degree of association of highly associated substances is lowered materially when they are dissolved in solvents possessing high dielectric constants. On the other hand, a solute of high dielectric constant must cause the depolymerization of the solvent, especially in concentrated solutions. Among soluble substances, inorganic salts are remarkable for their high dielectric constants. Thus,<sup>27</sup> the dielectric constant of potassium nitrate is 2.56; potassium chloride, 4.94; sodium nitrate, 5.18; sodium chloride, 6.12–6.29; and lead chloride, 4.20. At the first glance, it would seem that these dielectric constants are very small in comparison with that of water which is about 80. However, these values are for the solid state and, in the case of water, solidification causes the dielectric constant to decrease from 80 to 3.2.<sup>28</sup> It is apparent that all the above-named salts (except perhaps potassium nitrate) possess *higher* dielectric constants than does water, when considered in comparable states.

Walden<sup>29</sup> arrived at the same conclusion from measurements of dielectric constants of concentrated solutions.

Some of the theories of negative viscosity ascribed this effect to *electrostriction* due to the electrical charges on the ions. However, many facts are known which are quite incompatible with the conclusion from Drude and Nernst's<sup>30</sup> theory of electrostriction, that the total dissociation of one gram mol of every salt must cause the same contraction. Some salts give values very different from the mean, and many salts of ammonium, lithium, cesium, etc., even produce dilatation instead of contraction. This suggests the idea that changes in volume upon solution of other salts are also caused by other factors than electrostriction. The theory of electrostriction is based upon the assumption that every dielectric contracts under the influence of electrical polarization, if its dielectric constant increases under compression. All attempts, however, to observe

<sup>24</sup> Traube, *Phil. Mag.*, [6] 8, 158 (1904).

<sup>25</sup> Blanchard, *THIS JOURNAL*, 26, 1315 (1904).

<sup>26</sup> Bousfield, *Trans. Roy. Soc. (London)*, 206A, 101 (1906).

<sup>27</sup> Landolt-Börnstein, "Tabellen," 3rd ed., p. 766.

<sup>28</sup> Abegg, *Wied. Ann.*, 65, 229 (1898).

<sup>29</sup> Walden, *Bull. Acad. Sci. Petrograd*, 64, 305, 1055 (1912).

<sup>30</sup> Drude and Nernst, *Z. physik. Chem.*, 15, 79 (1894).

directly the compression of water under the influence of electrical charges, made by Quincke,<sup>31</sup> Roentgen<sup>32</sup> and Drude and Nernst,<sup>30</sup> proved unsuccessful. Therefore we cannot regard as established the existence of electrostriction and its depolymerizing action upon water. Depolymerization is rather the result of volume changes upon solution (decrease of water-concentration), of hydration and, especially in the case of dissolved salts, of the high dielectric constant of the solute.

It will now be shown that depolymerization is really able to lessen the internal friction of water, *i. e.*, to be the cause of "negative viscosity."

Applebey<sup>33</sup> stated that viscosity is increased by the presence of polymer molecules and, generally, of particles of large size, because (1) high values of viscosity are characteristic of associated liquids; (2) the viscosity of water falls more rapidly in the interval 0–50° with temperature increase than at higher temperatures, as heating produces here two effects which are additive, namely, the ordinary decrease of viscosity, and depolymerization which also tends to diminish viscosity; (3) pressure lowers the viscosity of water, as has been proved by Roentgen,<sup>34</sup> Warburg and Sachs,<sup>35</sup> Cohen<sup>36</sup> and others; (4) different ions change the viscosity of water in the reverse order of their mobilities.

The dependence of viscosity upon the size of particles can also be treated in a purely theoretical way. Einstein<sup>37</sup> has deduced from the fundamental equations of hydrodynamics a relation determining the viscosity  $\eta$  of a system composed of a liquid of the internal friction  $\eta_0$  and a great number of suspended solid spheres of a size very large in comparison with the particles of the liquid, the total volume  $\varphi$  of these particles being, however, but a small part of the volume of the liquid taken as unity.

$$\eta = \eta_0(1 + 2.5\varphi)$$

This equation has been tested on systems which best satisfy the named conditions, *i. e.*, on suspensions, and was brilliantly confirmed in some cases. Bancelin<sup>38</sup> in the laboratory of Perrin applied it with success to suspensions of various sized granules of gamboge in water. Experiments of Mifka<sup>39</sup> on weak colloidal solutions of noble metals also gave results which do not contradict this formula. In other cases such as the deter-

<sup>31</sup> Quincke, *Wied. Ann.*, 10, 521 *et seq.* (1880).

<sup>32</sup> Roentgen, *ibid.*, 11, 771 *et seq.* (1880).

<sup>33</sup> Applebey, *J. Chem. Soc.*, 97, 2020 *et seq.* (1910).

<sup>34</sup> Roentgen, *Wied. Ann.*, 22, 510 (1884).

<sup>35</sup> Warburg and Sachs, *ibid.*, 22, 518 (1884).

<sup>36</sup> Cohen, *ibid.*, 45, 666 (1892).

<sup>37</sup> Einstein, *Drude's Ann.*, 19, 289 (1906); 34, 591 (1911).

<sup>38</sup> Bancelin, *Compt. rend.*, 152, 1382 (1911); *Kolloid Z.*, 9, 154 (1911).

<sup>39</sup> Mifka, *Sitzb. Akad. Wiss. Wien, Abt. IIa*, 120, 1173.

minations of Wondstra,<sup>40</sup> Oden,<sup>41</sup> Freundlich and Ishizaka,<sup>42</sup> and Bingham and Durham<sup>43</sup> the observed values of  $\eta$  were higher than those calculated using the formula of Einstein, which is quite natural, as Einstein's formula was deduced under assumptions which are rarely satisfied, namely, the large relative size and the spherical form of the suspended particles, total absence of interaction between them and the medium, exceedingly small concentration, etc.

Einstein himself, however, made a successful attempt to apply his equation to a system of a notably different character, a solution of sugar in water. Combining this equation with his well-known formula of diffusion, he calculated the size of sugar particles and found the number of particles in a gram-molecule,  $N$ , to be  $6.56 \times 10^{23}$ , a figure which is in good accord with values obtained by the most reliable methods. It does not, therefore, seem too audacious to apply the equation of Einstein to solutions of salts in water and to water itself, as a system of large, associated molecules suspended in smaller simple water particles. It is clear that in such a case associated molecules, having larger values of  $\phi$ , cause a higher viscosity of the system. Upon their dissociation (or depolymerization),  $\phi$  falls, and with it  $\eta$ .

Jones<sup>44</sup> has put forward the opposite view, that the viscosity of water is increased by depolymerization owing to the increase of the "total frictional surface." This increase in frictional surface has been only assumed by Jones, but even if it should be proved, the conclusion of Jones could not be regarded as correct, as he connects the internal friction of a solution with the *surface* of particles which compose it, whereas the equation of Einstein, the only one having a serious theoretical basis,<sup>45</sup> shows that  $\eta$  of the solution is a linear function of the volume of the particles, not of their surface.

The same objection may be urged against Jones' theory of "negative viscosity" caused by salts, a property which he ascribes to the decrease of the "total frictional surface" owing to the introduction of large particles of salts into a solvent consisting of relatively small molecules.

7. The *depolymerization of the solute* by the solvent must be added to the factors influencing the viscosity of solutions. According to the above considerations, it can affect the viscosity in both directions, depending on the relative sizes of polymer and simple solute particles.

<sup>40</sup> Wondstra, *Z. physik. Chem.*, **63**, 619 (1908).

<sup>41</sup> Oden, *Nova Acta R. Soc. Upsala*, [7] **3**, No. 4, 103 (1913).

<sup>42</sup> Freundlich and Ishizaka, *Kolloid Z.*, **12**, 230 (1913).

<sup>43</sup> Bingham and Durham, *Am. Chem. J.*, **46**, 278 (1911).

<sup>44</sup> Jones and Veazey, **37**, *ibid.*, 405 (1907); Jones *et al.*, *Carnegie Inst. Pub.*, **80**, 207, 214, 225.

<sup>45</sup> Cf. a quite (formally) analogous equation of Hatschek, *Kolloid Z.*, **7**, 301 (1910), which is deduced by a different method.

The fact that water depolymerizes salts is beyond doubt. All osmotic methods show for salts dissolved in water molecular weights less than normal. This, indeed, is due to electrolytic dissociation, but if the salts in water should be highly associated, the sum of the molar weights should be greater than unity, as is the case for the same salts in non-aqueous solutions.

In the fused state, however, most salts are highly associated, as has been shown by Bottomley,<sup>46</sup> Walden<sup>47</sup> and others. Consequently, solution in water lowers their degrees of association, and depolymerization increases further with increasing dilution.

Arrhenius<sup>48</sup> states that depolymerization of solute always causes an increase of viscosity; the opposite phenomenon—coagulation (*i. e.*, aggregation of small particles into large ones) diminishes the viscosity of the solution, as has been shown for some suspensions by Wondstra<sup>49</sup> and Oden.<sup>41</sup>

This, however, is far from general. Freundlich and Ishizaka,<sup>42</sup> working on colloidal aluminum hydroxide, and Bingham and Durham,<sup>43</sup> working with suspensions of infusorial earth and graphite, have found an enormous increase of viscosity to take place upon coagulation. Changes of viscosity in the same direction have been found by Biltz and Vegesack<sup>49</sup> for some aniline dyes and by Friedlaender<sup>50</sup> for emulsions of butyric acid in water. This shows that upon coagulation different substances undergo volume changes in opposite directions. Moreover, many conditions may act indirectly, such as the decrease of accuracy of determinations owing to the clinging of suspended particles to the walls of the capillary tube, electrical phenomena, form changes, etc.

If all such factors could be subjected to quantitative estimation, calculation of the viscosity of a solution might be attempted. The present state of our knowledge, however, does not allow this to be done, and all attempts to make such a calculation over a wide range of concentration, using one or two of the named factors only, have proved unsuccessful.<sup>51</sup>

It has been necessary, therefore, to limit this paper to qualitative considerations only, concerning the causes of the increase or decrease of the internal friction of solvents by solutes, and a determination of which of the enumerated factors of the viscosity of solutions are able to account for the phenomenon of "negative viscosity."

The viscosity of a solute, mentioned in the last paragraph, cannot be used for this purpose, as it can act in both directions and even for the less

<sup>46</sup> Bottomley, *J. Chem. Soc.*, 83, 1421 (1903).

<sup>47</sup> Walden, *Z. Elektrochem.*, 14, 715 (1908).

<sup>48</sup> Arrhenius, *Biochem. J.*, 11, 112 (1912).

<sup>49</sup> Biltz and Vegesack, *Z. physik. Chem.*, 73, 500 (1910).

<sup>50</sup> Friedlaender, *ibid.*, 38, 430 (1901). Rothmund, *ibid.*, 63, 54 (1908).

<sup>51</sup> See the works of Applebey, Ref. 33; Einstein, Ref. 37; Grüneisen, *Wiss. Abhandl. Reichsanstalt*, 4, 237 (1905); Bousfield, Ref. 26.

viscous salts exceeds by many hundred times the viscosity of water. Thus, ammonium nitrate has been shown to have the coefficient of internal friction  $\eta = 2.477$  abs. units at  $162^\circ$ , while the viscosity of water from the data of DeHaas<sup>52</sup> at  $142^\circ$  and  $153^\circ$ , is calculated by extrapolation to  $162^\circ$  to be 0.00172, *i. e.*, 1440 times lower.

The depolymerization of the salt by water can lower the viscosity of the solution, but only in comparison with the salt in the liquid state and not with the solvent. If we assume, indeed, in the case of ammonium nitrate dissolved in water, a very high degree of association of the salt, its total depolymerization by water, and the largest imaginable influence of depolymerization upon the viscosity of the solute, assuming total depolymerization to diminish the viscosity as much as 10 times, we shall find the theoretical liquid component of the solution to be still 140–150 times more viscous than water. This is true notwithstanding the fact that salts lower the viscosity of water in an indirect way when they are present in a sufficiently small amount. At higher concentrations their own high viscosity predominates, and "negative viscosity" is no longer observed.

Of the other factors, hydration and the electrical field of ions are able only to increase, not to diminish, the initial viscosity of water, as has been said above. The decomposition of complexes can diminish the internal friction in some cases, but only with regard to the solute, which at sufficiently great dilutions forms but a small part of the whole solution. Only the *depolymerization of the solvent, i. e.*, of the component quantitatively prevailing in the solution and therefore materially influencing its viscosity, is able to produce *by itself* negative viscosity.<sup>53</sup> Other factors can favor or hinder and, in many cases, overbalance it, giving rise even to a positive viscosity effect.

ODESSA, RUSSIA

<sup>52</sup> De Haas, Comm. Leyden, No. 12 (Landolt-Börnstein "Tabellen," 3rd ed., p. 76).

<sup>53</sup> The important part played by depolymerization has been acknowledged by many authors and most clearly expressed by Kraus. Our views about negative viscosity are in full accord except for the causes of depolymerization, which Kraus ascribes principally to the action of Tammann's "Binnendruck."

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## A CENTRIFUGAL METHOD FOR PREPARING COLLOIDAL FERRIC HYDROXIDE, ALUMINUM HYDROXIDE AND SILICIC ACID

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The two methods which have been most used for the preparation of electrolyte-free colloidal ferric hydroxide and aluminum hydroxide are in many respects unsatisfactory. The first, in which the hydroxide is formed by the hydrolysis of the acetate and the acetic acid removed by vigorous boiling was first proposed by Crum<sup>1</sup> in 1853 for preparing colloidal aluminum hydroxide. Crum failed to prepare colloidal ferric hydroxide by this method but Péan de Saint-Gilles<sup>2</sup> succeeded in doing so in 1855. The second method is based upon the peptization of the freshly precipitated hydroxides by their respective chlorides. The excess of electrolytes in this case is removed by dialysis. This method was first used by Graham<sup>3</sup> in 1862.

The disadvantages offered by each of these methods are numerous. Either prolonged boiling or prolonged dialysis is necessary to remove the excess of electrolyte. The removal of electrolyte is always far from complete. Graham was never able to remove the last 1.5% of hydrochloric acid from his sol by dialysis, though Nicolardot<sup>4</sup> succeeded in reducing the content to 0.16%. Neidle and Barab<sup>5</sup> by hot dialysis obtained sols of ferric hydroxide containing 38.7 gram equivalents of ferric iron to 1 gram equivalent of chlorine. Péan de Saint-Gilles was unable to remove all of the acetic acid from his sol for he found that if the boiling were carried too far precipitation would result. The degree of dispersion obtained varies widely. That of the Graham colloid changes on standing. It is almost impossible to make up successive sols with duplicated properties. This is shown by the widely different properties attributed to each by different investigators. Both require low concentrations for stable sols. Crum recommended a concentration of not over 0.1% for aluminum oxide.

Weiser<sup>6</sup> improved the method of Crum and Péan de Saint-Gilles by adding only enough acetic acid to the thoroughly washed, freshly precipitated hydroxides, to peptize them. The amount of acetic acid required was

<sup>1</sup> Crum, *Ann.*, 89, 168 (1853).

<sup>2</sup> Saint Gilles, *Compt. rend.*, 40, 568 (1855).

<sup>3</sup> Graham, *J. Chem. Soc.*, 15, 250 (1862).

<sup>4</sup> Nicolardot, "Recherches sur les sesquioxide de fer." *Thesis*, Paris, 1905.

<sup>5</sup> Neidle and Barab, *This Journal*, 39, 80 (1917).

<sup>6</sup> Weiser, *J. Phys. Chem.*, 24, 30, 277 (1920).



considerably less than that necessary to form the normal acetates and he found that vigorous boiling for from 25 to 40 hours was sufficient to remove the excess of acid.

In both the Graham method and the method of Weiser the freshly precipitated hydroxides are used as a basis for the sol, peptization being effected in the first case by the hydrochloric acid formed in the hydrolysis of the chloride, and in the second case by the addition of small amounts of acetic acid. It is well known that both ferric and aluminum hydroxides may be peptized to a certain extent merely by the removal of the precipitating agent by thorough washing with distilled water. The washing of these precipitates through the filter, which frequently happens in quantitative analyses, is an example of this. Weiser made a comparative test of the peptizing power of the various acids and of water on aluminum hydroxide. He found that 0.508 g. out of 0.750 g. or about 68% was peptized by 5 cc. of 0.2 *N* acetic acid while 0.477 g. out of 0.750 g. or about 63% was peptized merely by repeated washings with distilled water.

**Principle Underlying the Present Investigation.**—The above data indicate that thorough washing is about as effective a peptizing agent as dilute acids. If complete peptization could be effected by thorough washing it would appear to have two distinct advantages over the peptization by means of acids: (1) the removal of the electrolyte set free in the precipitation of the hydroxides ( $\text{NH}_4\text{Cl}$ ) would be more complete, for Weiser and Graham were obliged to discontinue the washing as soon as peptization started; (2) the addition of a peptizing agent and its consequent imperfect removal by prolonged dialysis or boiling would be unnecessary.

Several investigators have demonstrated the possibility of throwing colloidal particles out of solution by means of a high centrifugal force.

Franklin and Freudenberger<sup>7</sup> separated the colloidal particles of platinum and prussian blue from their respective sols by prolonged application (6–7 hours) of a centrifugal force of 1520 times gravity.

Friedenthal<sup>8</sup> in 1909 succeeded in separating the casein from cows' milk by centrifugal force. Perrin,<sup>9</sup> by fractional centrifuging, prepared sols of gamboge having particles of fairly uniform size. He failed, however, to fractionate colloidal ferric hydroxide by this means.

These results indicate the possibility of removing additional amounts of electrolyte from a solution by washing even after it has become colloidal.

A Sharples Laboratory Supercentrifuge, operated by an electric motor at 32,500 revolutions per minute, has been used in this laboratory for the past year for the separation of a highly hydrated emulsoid complex from

<sup>7</sup> Franklin and Freudenberger, *Trans. Am. Electrochem. Soc.*, 8, 29 (1905).

<sup>8</sup> Friedenthal, *Kolloid Z.*, 15, 75 (1914).

<sup>9</sup> Perrin, "*Les Atomes*," Libraire Felix Alean, 1914, 135.

suspensions of a heavy clay subsoil. It was considered probable that by means of this machine washing could be continued until enough of the precipitating agent was removed to make possible the existence of the hydroxides in a stable colloidal condition, comparatively free from electrolytes and of a relatively high concentration.

### Experimental

**Removal of Deposit from the Centrifuge Bowl.**—In the earlier work with the centrifuge the material deposited in the bowl was removed by scraping with a long spatula. On account of the small diameter of the bowl (5 cm.) this method was found very unsatisfactory when one wished to remove the total content very carefully and in the exact order in which it was deposited. This difficulty was overcome by means of a device made as follows. The inside diameter of the bowl was carefully measured, its circumference calculated, and a rectangular piece of celluloid prepared which was of the same length as the inside depth of the bowl and the same width as its circumference. This was rolled up and slipped into the bowl. Its natural resilience held it firmly against the walls, forming a uniform celluloid lining or sleeve. After making a run, the bowl bottom was removed, a long, narrow (6 mm.), sharply pointed spatula slipped between the sleeve and the bowl and worked around the entire circumference. This loosened the sleeve so that it could be removed by seizing the two edges at the seam with a small pair of pliers and exerting a steady pull. By unrolling the sleeve the entire contents of the bowl become visible. Division of the deposit could be made at any point at which its appearance indicated advisable and the entire deposit removed almost quantitatively by means of a spatula.

#### 1. Preparation of the Iron Hydroxide

In preparing the colloidal ferric hydroxide, ammonium hydroxide was added to a concentrated solution of ferric chloride (slowly as the neutral point was being approached) with constant stirring until minute floccules of ferric hydroxide were barely visible. The more granular precipitate formed by adding an excess of ammonium hydroxide was found to be more slowly reversible than that obtained by the above procedure. The precipitate was allowed to settle and was washed by decantation until it commenced to become colloidal. This solution was then passed through the centrifuge at the rate of about 3 liters per hour. At the end of the run the sleeve was found to be coated with an extremely finely divided layer of reddish-brown ferric hydroxide. This material was removed, placed in a mortar with a little water, then mixed to a uniform paste with the pestle. This procedure facilitated the uniform dispersion of the oxide when it was poured into a large bulk of water for the next washing. After being thoroughly washed on the mechanical shaker with 1 to 2 liters of water the suspension was passed through the centrifuge a second time at a somewhat slower rate than at first. After this process had been repeated four times, the contents of the bowl could be divided into two distinct parts, (1) a yellowish-brown, fairly stiff deposit on the lowest 5 cm. of the sleeve which graded slowly into (2) a dark red, highly hydrated, semifluid deposit which was barely stiff enough to adhere to the sleeve

when it was removed with considerable care. The deposit of the dark red oxide was fairly uniform over the upper three-fourths of the sleeve.

The material was divided into two fractions: Sol A, which included all the yellowish-brown oxide from the bottom of the bowl up to the point where the dark red material was apparently homogeneous, and Sol B, the dark red material. Sufficient water was added to each of these separates to bring them to such a consistency that they could be readily removed and measured by means of a pipet. The strength of the sols was then determined by evaporating 10 cc. to dryness on a water-bath, drying at  $105^{\circ}$  and weighing. After being standardized, these were used as stock solutions for making up sols of any desired concentration. The liquid which was discharged on the fourth and subsequent washings (Sol C) was a beautiful cherry-red sol which gave no reaction for ionic iron with thiocyanate or ferrocyanide and only a very slight opalescence when dissolved in nitric acid and tested for chlorides with silver nitrate.

**Purity and Solubility.**—Sol B when dissolved in nitric acid likewise gave only a barely perceptible opalescence with silver nitrate. Its color was not changed by the addition of a few drops of potassium thiocyanate. A dirty brown precipitate was formed by potassium ferrocyanide which assumed a greenish tinge on standing. The addition of one drop of *N* hydrochloric acid produced the intense blue color characteristic of the ferric iron. When poured into concentrated acid in the cold, the colloid flocculates, but on heating, the coagulum readily dissolves.

Another sample was washed seven times by means of the centrifuge and analyzed for chlorides. One gram equivalent of chlorine was found to every 396 gram equivalents of ferric iron. The amount of chlorine could doubtless be still further reduced by additional washings.

**Stability.**—All three sols are stable on standing. If the first 2 cm. of material in the bottom of the bowl is discarded none of the material in Sol A, which contains the largest particles, is thrown down by 20 minutes' centrifuging in a centrifuge of the ordinary tube type making 2,000 revolutions per minute.

By boiling on the water-bath the sols may be reduced to an almost syrupy consistency but may be restored to their original concentration by the addition of water. A large part of the material may be rather easily brought back into colloidal condition even after evaporation to dryness.

**Color of Sols.**—The color of the sols is influenced by at least three factors: concentration, size of particle, and depth of the liquid examined. In the concentrated stock solutions Sol A is yellowish-brown, B is reddish-brown, and C slightly more reddish than B. On dilution to the proper extent all may be brought to a red color, on still further dilution all appear yellow. This holds, of course, for the Graham and Péan de Saint-Gilles colloids as well. All three sols are turbid in reflected light when fairly

concentrated. Sols B and C are clear in concentrated solutions when examined through transmitted light; Sol A is distinctly turbid in concentrated solutions and slightly so even in fairly dilute solutions.

**Color of Coagulum.**—Because of the influence of concentration on the color of the sols it was found that the color of the coagulum was a better indication of the relative colors of the particles in the sols. Five cc. each of Graham's, and Péan de Saint-Gilles' colloids and of Sols A, B, and C were placed in test-tubes and flocculated by means of aluminum sulfate. There was a remarkably uniform gradation in color from the brownish red of the Graham colloid through the lesser red of the Péan de Saint-Gilles colloid to the yellowish brown of Sol A. From the fact that Sol A was made up of that fraction of the oxide which was deposited first in the bowl of the centrifuge, we should assume that it was made up of the largest and least hydrous particles. Sol B which was made up of that fraction deposited in the top of the bowl would be naturally made up of somewhat smaller particles than A. Sol C whose particles were not thrown down by the centrifugal force used to throw out the others would be expected to be the most highly dispersed of the three. On the other hand, we should expect that the Graham colloid, which in this case was prepared by pouring a solution of ferric chloride into boiling water, conditions favoring extremely rapid hydrolysis, would be the most highly dispersed of the lot. Sols A, B, and C would be expected to be less highly dispersed since they were formed by peptizing the almost visible floccules by the removal of the flocculating ion. These results bear out the work of Weiser and others that the color of hydrous iron oxide may vary from red to yellow depending upon the size of the particles.

## II. Preparation of the Aluminum Hydroxide Colloid

Sols of aluminum hydroxide have been prepared in a way similar to that used for ferric hydroxide by the thorough washing of the hydroxide precipitated from aluminum chloride by ammonium hydroxide. Since there is less tendency for aluminum hydroxide to come down in the granular, more slowly reversible form, it is not necessary to control so carefully the amount of the precipitating agent. The addition of ammonium hydroxide to a slight excess will give good results.

The color of the concentrated stock solutions ranges from white in the case of Sol A to bluish-white in the case of Sols B and C. A is turbid in transmitted light, B and C are clear.

The reactions of the aluminum sols to heat and acids are similar to those described for iron.

**Sensitiveness to Polyvalent Ions.**—The early work on the preparation of colloidal aluminum hydroxide is full of references to its extreme sensitiveness to polyvalent electrolytes.<sup>1</sup> Previous investigations<sup>10</sup> have indi-

<sup>10</sup> Rose, *Kolloid Z.*, 15, 1(1914). Weiser, *J. Phys. Chem.*, 24, 277(1920).

cated that the precipitation of colloidal aluminum hydroxide by sulfates is distinctly different from the precipitation by chlorides or nitrates, in that repeated washings fail to remove enough of the precipitating agent to allow the precipitate to assume colloidal condition. This stimulated a desire to find out whether the more thorough washing used in this investigation would bring back the precipitate from the sulfate into a stable colloidal condition.

A concentrated solution of aluminum sulfate was precipitated with a slight excess of ammonium hydroxide and allowed to stand for one week. The supernatant liquid was poured off, distilled water added to replace it and the precipitate thoroughly broken up by stirring and by shaking in a mechanical shaker for 15 minutes. The suspension was then passed through the centrifuge as rapidly as possible (1 liter per minute). All the oxide was found in the lower fourth of the bowl. This was removed and mixed to a pasty consistency in a mortar with a little water. This paste was then poured into a bottle containing 2 liters of water, shaken as above described and centrifuged. This time the aluminum hydroxide was found deposited higher up in the bowl, indicating that a longer application of centrifugal force had been necessary to throw it down. After the second washing it was found necessary to cut down the rate of flow through the centrifuge to 4 liters per hour in order to throw out the bulk of the aluminum hydroxide. With the fourth washing the rate was reduced to 2 liters per hour; and some aluminum hydroxide was so finely dispersed that even this application was insufficient to throw it out of suspension.

When the celluloid sleeve was removed after the fourth washing, the upper two-thirds of it was found to be coated to a depth of 2 mm. with a transparent, gelatinous, deposit of aluminum hydroxide which appeared bluish-white when removed with a spatula. This material was found to be readily miscible with water in all proportions, forming a beautiful bluish-white sol which seemed as stable as that formed, from the chloride. All of the sulfate ion was not removed, for when a little of the concentrated sol is dissolved in hot nitric acid and barium chloride solution added, on standing a few crystals of barium sulfate are formed. Whether any more sulfate can be removed by further washing is yet to be determined; but the results seem to show conclusively that the sulfate ion is not so strongly adsorbed by the precipitated aluminum hydroxide but that it may be sufficiently removed by washing to allow the aluminum hydroxide to go into a stable colloidal condition. It also indicates that the previously termed "irreversibility" is due to the adsorption of sulfate rather than to the formation of a definite chemical compound, which is in accord with the views of Bancroft and of Weiser.<sup>11</sup>

<sup>11</sup> Weiser, *J. Phys. Chem.*, 24, 277 (1920).

### III. The Preparation of Colloidal Silicic Acid

Silicic acid sols are generally prepared by pouring a solution of sodium silicate into an excess of dil. hydrochloric acid.<sup>12</sup> The sodium chloride formed and the excess of acid are removed as far as possible by dialysis. Dialysis is usually considered complete when the wash water yields no test for chlorides with silver nitrate. Such sols have a strong tendency to gelatinize and gelation is so difficult to revert that it has commonly been considered irreversible. Several other methods of preparation also have been used.<sup>13</sup>

The preparation of a sol of aluminum hydroxide from the "irreversible" precipitation of the hydroxide in an excess of sulfate ions by the washing out of the precipitating agent indicated the possibility that the irreversibility of silicic acid gels might be of the same character. Silicic acid was precipitated by slowly adding dilute hydrochloric acid (1:3) to dilute (1:3) commercial sodium silicate. Precipitation occurred before neutralization so the solution was still slightly alkaline. The precipitate was washed by decantation until most of the chloride was removed, then all lumps were carefully broken up and the mixture was passed through the centrifuge at the rate of one liter per minute. The washing of the precipitate was continued until practically all of it had been converted into the colloidal condition. This occurred after 15 washings. Table I gives detailed data on these washings. The first column shows the number of washings, the second the rate at which the suspension was passed through the centrifuge, the third the approximate amount of silicic acid thrown down, the fourth the total volume of wash water used, the fifth column shows the degree of alkalinity of the wash water expressed in terms of the number of cubic centimeters of 0.2 *M* hydrochloric acid necessary to neutralize 100 cc. of the wash water up to the sixth washing. Thereafter the alkalinity is expressed in terms of hydrogen-ion concentration determined colorimetrically by the method of Gillespie using thymol blue as indicator.

It was necessary to cut down the rate of addition from 1000 cc. per minute to 350 cc. per minute after the first washing in order to throw down the more highly dispersed material. After the third washing a sol of fair concentration was obtained. After four washings the rate of feed was cut to  $\frac{1}{10}$  the original value and still a considerable amount of the silicic acid was left in suspension. Practically all chlorides were removed after the sixth washing, but the wash water was still alkaline ( $P_H$  9.7). After 15 washings the wash water was still alkaline and the hydrogen-ion concentration did not seem to decrease further as long as

<sup>12</sup> Graham, *Phil. Trans.*, 151, 183 (1861).

<sup>13</sup> Berzelius "Lehrbuch," 3rd ed., vol. 4, II, pp. 5, 122 (1833).

G. Crimaux, *Compt. rend.*, 98, 105 (1884).

Desch, "The Chemistry and Testing of Cement," 1911, 58.

TABLE I  
WASHING THE SILICIC ACID PRECIPITATE

Washing	Rate Cc. per min.	Precipitate Bowls full	Total volume of water Cc.	Alkalinity of wash water Cc.	Nature of wash water discharged
1	1000	7	5500	5.2	Fairly clear
2	350	6	4000	5.0	Slightly opalescent
3	200	5	4000	5.8	Very opalescent
4	200	4.5	4000	5.6	Considerable silicic acid in colloidal condition
5	100	4	4000	4.4	
6	100	3	3000	1.7	Practically free from chlorides
				$P_H$	
7	100	3	2000	9.7	Clear bluish-white sol.
8	100	2.5	2000	9.5	
9	100	2	2000	9.4	
10	100	1.7	1500	9.3	
11	100	1.5	1500	9.1	
12	100	1	1000	8.8	
13	100	1	1000	9.0	
14	100	0.75	1000	8.8	
15	100	0.5	1000	8.8	

washings were continued on the coarser non-colloidal material. The last four washings showed a hydrogen-ion concentration equivalent to  $P_H$  8.8.

The sols discharged on the tenth and subsequent washings were poured together yielding a mixture with a Sørensen value of 9.0. One liter of this mixture was acidified by adding 7 cc. of 0.2 *M* hydrochloric acid. It was found possible to throw down the bulk of this colloidal silicic acid by prolonging sufficiently the application of the centrifugal force. This was accomplished by cutting down the rate of addition to 25 cc. per minute. As the capacity of the bowl was approximately 300 cc. each part of the sol was subjected to a centrifugal force 30,000 times gravity for 12 minutes. The silicic acid thrown down was resuspended in a liter of distilled water and washed again. The effect of the repeated washings on the hydrogen-ion concentration of the wash water is shown in Table II.

TABLE II  
WASHING THE ACIDIFIED SOL OF SILICIC ACID  
Rate, 25 cc. per minute

Washing	$P_H$	Washing	$P_H$	Washing	$P_H$
1	4.0	4	6.4	6	6.5
2	5.8	5	6.5	7	6.5
3	6.0				

The Sørensen value was readily reduced to 6.5 but seemed to be constant at that point.

Another fraction of the alkaline sol was washed using the same rate of feed as in Table II, but no acid was added. The results of this experiment are presented in Table III.

TABLE III  
WASHING THE DISCHARGED SOL  $P_H$  9.0  
Rate, 25 cc. per minute

Washing	$P_H$	Washing	$P_H$	Washing	$P_H$
1	9.0	3	7.1	5	6.5
2	8.4	4	6.5	6	6.5

When this highly dispersed silicic acid was thrown down and repeatedly washed the hydrogen-ion concentration was readily reduced to the Sørensen value 6.5 which is identical with the value obtained when approached from the acid side. Since 6.5 seems to be the final constant value obtained whether approached from the acid or the alkaline side, it seems quite probable that this represents approximately the true Sørensen value of the colloidal silicic acid.

**Physical Properties.**—When the celluloid sleeve was removed after the deposition of the highly dispersed silicic acid it was found to be covered at the bottom with a rather stiff greasy white deposit which became clear and transparent and semifluid at the upper end of the bowl. In the middle of the bowl the deposit was transparent and very sticky. This material was divided into two fractions, one consisting of the white material (Sol A) and the other the more fluid transparent material (Sol B). Both were readily dispersed in distilled water forming bluish-white, very stable sols. By heating on the water-bath the sol can be concentrated to an almost syrupy consistency which can be brought back to the original sol condition by the restoration of the original water content. If the boiling is carried too far minute needle-like crystals of silicic acid separate. The sols show no tendency whatsoever to gel even in the highest concentrations. Mixtures of equal volumes of 0.2 *M* hydrochloric acid and of 0.2 *M* sodium hydroxide solution and 0.2% silicic acid are perfectly stable. Some of the silicic acid apparently goes into true solution in the alkali on long standing.

**Purity of the Sol.**—As noted above the sol appeared free from chlorides after 6 washings. This test was made by precipitating the silicic acid with aluminum sulfate and then treating the clear supernatant liquid with silver nitrate. This test is open to the objection that there may have been present minute traces of chlorides which were carried down by the precipitated silicic acid. A further test was made on the sol having a Sørensen value of 6.5 by adding a little sodium carbonate to 100 cc. of the sol to neutralize any free hydrochloric acid, then evaporating to dryness on the water-bath. The silicic acid was still further dehydrated by heating for 2 hours in the oven at 105°. It was then digested with



nitric acid, diluted and the supernatant liquid tested with silver nitrate. The test was negative. Similar tests on standard sodium chloride solutions show that under the conditions of the test the presence of 1 part of chlorine in 4,000,000 of sol could have been detected. This result was to have been expected from the effects of the repeated washings on the reaction of the sol. The hydroxyl ion is considered highly adsorbed by silicic acid and the fact that it was so completely removed as to enable the sol to yield a slightly acid reaction is additional evidence of the thoroughness of the removal of impurities by repeated washings.

While thus far the method outlined has been used only for the preparation of colloidal ferric and aluminum hydroxides and silicic acid it would appear that with perhaps slight alterations in procedure a large number of sols of similar substances might be prepared.

The writer is indebted to Professors M. F. Miller and W. A. Albrecht for suggestions and criticisms.

### Summary

1. A method is described for preparing colloidal ferric hydroxide, aluminum hydroxide and silicic acid from the fresh precipitates of these substances by the removal of the excess of precipitating agent by thorough washing by means of a supercentrifuge.

2. This method appears to have certain advantages over the older methods: (a) the removal of the electrolytes formed on precipitation is more complete; (b) the addition of a peptizing agent and its consequent incomplete removal by either prolonged dialysis or boiling is unnecessary; (c) sols of a more uniform degree of dispersion can be prepared, since particles of similar size and of similar degrees of hydration are deposited in the same zone in the centrifuge bowl; (d) sols of any desired concentration from a semi-gel to the merest trace can be prepared by the addition of water to the more concentrated form, and all concentrations are very stable; (e) while the method thus far has been used for the preparation of colloidal iron and aluminum hydroxides and silicic acid only, it would appear that with perhaps slight alterations in the procedure a large number of sols of similar substances might be prepared.

3. Aluminum hydroxide precipitated by ammonium hydroxide in the presence of an excess of sulfate ion is not irreversible.

COLUMBIA, MISSOURI

[CONTRIBUTION FROM THE PACIFIC EXPERIMENT STATION, U. S. BUREAU OF MINES]

## EQUILIBRIA IN THE SYSTEMS IRON:CARBON:OXYGEN AND IRON:HYDROGEN:OXYGEN, AND THE FREE ENERGIES OF THE OXIDES OF IRON<sup>1</sup>

By E. D. EASTMAN<sup>2</sup>

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A review of the published researches on the gas-solid equilibria in the above important systems, and of the literature concerning the oxides of iron reveals a surprising degree of confusion. The results of different investigators are not always in satisfactory agreement and are often difficult of interpretation. Some of the more recent experiments, however, indicate a few of the causes of difficulty, and remove certain phases of the subject from the realm of hypothesis. While exact knowledge of these systems must remain incomplete until further work has been done, it appears that an adequate basis exists for the determination of equilibrium constants and free energies with a certainty and accuracy sufficient for many scientific and technical purposes. In the following the numerical results of such determinations will be presented, preceded by a critical discussion and summary of the experimental data upon which they rest.

### One and Two Component Systems

The polymorphism of elementary iron has been ignored throughout the following work, as the equilibrium data are in no case of enough accuracy to require a distinction between the different forms which are stable in the various temperature ranges.

The equilibria in which solid carbon appears are perhaps slightly influenced by the form in which this substance occurs. Such variations are in general small<sup>3</sup> and will be neglected here. Graphite is the stable phase into which "amorphous" forms in these equilibria are slowly changing, and to which the final free energy calculations are referred.

In the system iron: carbon the compound  $\text{Fe}_3\text{C}$  and solutions of it or of carbon in iron are known in the solid state. Owing to the difficulties of experimental investigation the solubility limits and temperatures and even the qualitative nature of the iron-carbon diagram are rather uncertain.  $\text{Fe}_3\text{C}$  does not appear in the equilibrium diagram of the "stable system" given in the Landolt-Börnstein "Tabellen." In the "unstable system" it does occur as a separate phase, but below  $700^\circ$  is represented

<sup>1</sup> Published by permission of the Director of the U. S. Bureau of Mines. The review and calculations presented here were made in connection with a theoretical study of the reducing efficiency of fuel gases upon the oxides of iron for the Southwest Experiment Station of the Bureau of Mines, at Tuscon, Arizona.

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<sup>3</sup> See for example, the discussion of Falcke's work below.

as not soluble in iron. The instability of cementite is further indicated by the thermochemical datum of Ruff and Gersten,<sup>4</sup> who find an absorption of 15,000 cal. per mol in its formation from the elements. It has been assumed in the following that  $\text{Fe}_3\text{C}$  is not one of the phases which must be considered in the study of stable equilibria, though iron-carbon solutions may be present.

The equilibrium of hydrogen with iron has been studied by Sieverts.<sup>5</sup> No separate hydride phase is formed, and the solubility of hydrogen is so small that the activity of solid iron cannot be appreciably affected by it. It is, therefore, not a factor in the iron: hydrogen: oxygen system.

The compounds  $\text{Fe}_2\text{O}_3$  and  $\text{Fe}_3\text{O}_4$  seem to be sufficiently well established as chemical individuals. Polymorphism is found<sup>6</sup> in the case of each of these oxides. Of especial interest are the magnetic inversions in hematite at about  $678^\circ$  and in magnetite, variously given as between  $525^\circ$  and  $581^\circ$ .

The dissociation pressures of the compound  $\text{Fe}_2\text{O}_3$  have been experimentally studied by Sosman and Hostetter.<sup>7</sup> They directly determined the pressure-composition curves between  $\text{Fe}_2\text{O}_3$  and  $\text{Fe}_3\text{O}_4$  at  $1100^\circ$  and  $1200^\circ$ . These curves are shown in Fig. 1. Their form indicates a continuous series of solid solutions of the oxides in each other at both temperatures.

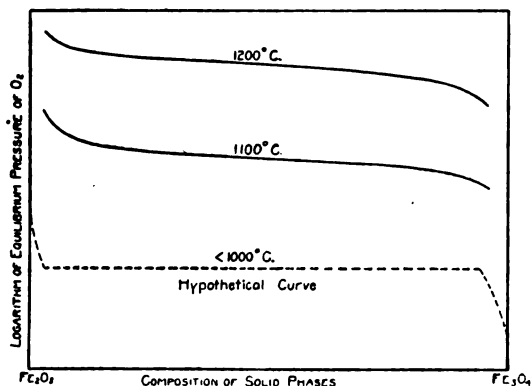


Fig. 1.—Equilibrium pressures in the system Fe: O.

slopes more and shows less tendency to discontinuity than that at  $1100^\circ$ . This would not be the case, it is believed, if the explanation of Smits and Bijvoet were correct, but would be expected if the oxides were soluble in all proportions. Sosman and Hostetter actually prepared, at  $1200^\circ$ , various solutions intermediate between  $\text{Fe}_2\text{O}_3$  and  $\text{Fe}_3\text{O}_4$  which remained homogeneous, as shown by their optical properties, even at atmospheric temperatures. The persistence of such solutions does not, however,

<sup>4</sup> Ruff and Gersten, *Ber.*, **45**, 63 (1912); **46**, 394 (1913).

<sup>5</sup> Sieverts, *Z. physik. Chem.*, **77**, 591 (1911).

<sup>6</sup> Sosman, *J. Washington Acad. Sci.*, **7**, 55 (1917).

<sup>7</sup> Sosman and Hostetter, *THIS JOURNAL*, **38**, 807, 1188 (1916).

<sup>8</sup> Smits and Bijvoet, *Proc. Acad. Sci. Amsterdam*, **21**, 386 (1919).

preclude the possibility that they are unstable (supersaturated) at low temperatures. The approach of the pressure-composition curve to the two-phase type is very close even at 1100°. It seems probable, therefore, that a separation into distinct phases occurs, in the equilibrium case, at temperatures a few hundred degrees lower. This hypothetical behavior, also suggested by Smits and Bijvoet, is illustrated by the dotted curve of Fig. 1.

The methods which have been proposed in the literature for the preparation of ferrous oxide (FeO) do not give a pure product, as has been shown by Hilpert and Beyer.<sup>9</sup> In very careful experiments these workers failed to obtain ferrous oxide free from ferric oxide by reducing higher oxides in a stream of hydrogen and water vapor or carbon monoxide and carbon dioxide of proportions such that ferro-ferric oxide but not ferrous oxide should be reduced. They attribute their failure to the formation of solid solutions between ferrous and ferro-ferric oxides. Matsubara's experiments (*vide infra*), do show ferro-ferric oxide to be soluble to some extent in ferrous oxide. Hilpert's results may have been due to this, but could equally well be explained by the instability of ferrous oxide with respect to ferro-ferric oxide and iron below some definite temperature. This behavior was anticipated as a possible cause of difficulty by Sosman<sup>7</sup> and by Smits and Bijvoet.<sup>8</sup> It is apparent from the form of the equilibrium curve of Fig. 3 below, and has recently been independently verified in qualitative experiments by Chaudron.<sup>10</sup> When, therefore, ferrous oxide is prepared at a high temperature, on cooling it reacts in part according to the equation



and the product will always show more or less ferric iron on analysis, the amount depending on the rapidity of cooling of the sample. More concerning this reaction and solid solution among the oxides will be said later.

### The System Iron:Carbon:Oxygen

Braithwaite<sup>11</sup> was able to establish in a qualitative way the reversibility of the reaction of carbon monoxide upon ferro-ferric oxide. He also showed that carbon monoxide is nearly completely oxidized to the dioxide by ferric oxide at "low red heat."

Baur and Glaessner<sup>12</sup> were the first to publish quantitative results in this field. They undertook to determine the equilibrium composition of gas in the reactions

<sup>9</sup> Hilpert and Beyer, *Ber.*, **44**, 1608 (1911).

<sup>10</sup> Chaudron, *Compt. rend.*, **172**, 152 (1921); *Ann. chim.*, **16**, 221 (1921).

<sup>11</sup> Braithwaite, *Chem. News*, **72**, 211 (1895).

<sup>12</sup> Baur and Glaessner, *Z. physik. Chem.*, **43**, 354 (1903).



and



In outline their methods follow.

Two g. of a mixture of ferro-ferric oxide (79.06%) and ferrous oxide (20.94%), prepared by reducing pure ferric oxide in a stream of hydrogen and treating the resulting iron with carbon dioxide at 600°, was placed in a porcelain boat in an electrically heated glazed porcelain tube which was connected to a mercury buret and a pump. After evacuation, the tube was filled either with carbon monoxide or dioxide and maintained at constant temperature, measured by a thermocouple in the tube near the boat, for periods varying mainly from 12 to 24 hours. The gas was then withdrawn and analyzed for carbon monoxide and dioxide. The ferrous oxide-iron mixtures were obtained by repeated treatment of the above preparation with carbon monoxide at 800°, the procedure being otherwise the same. The time of each run appears to have been more or less arbitrary, the degree of concordance of results approaching equilibrium from both sides being relied upon to determine whether reaction had been completed in the time allowed.

An inspection of the points representing their work, in Fig. 3, leaves little doubt that at the higher temperatures equilibrium was really attained. At 600° and below, the observations in the ferrous oxide-iron system deviate widely from the general mean, due in part perhaps to extreme slowness of reaction at these temperatures.

Schenck, Semiller, and Falcke<sup>13</sup> have published data relating to systems in which in addition to iron and ferrous oxide, solid carbon was present.

The solid phases were prepared by reduction of ferrous oxalate in a stream of hydrogen at 650° and passing carbon monoxide over the reduced metal for 4 hours at 800°. About 10 g. of the mixture so obtained, probably containing considerable quantities of each of the phases, iron, ferrous oxide, carbon, was used in each experiment. The mixture being studied was contained in a porcelain bulb kept at constant temperature, measured by a calibrated Le Chatelier thermocouple near the bulb in the furnace, and the progress of the reaction followed by observing the total pressure. When the pressure became constant, equilibrium was assumed to have been established and a sample of gas was then withdrawn and analyzed.

The composition of gas fixed by such a procedure should be the same in the presence of solid carbon as without it, provided that iron and ferrous oxide phases are present and active in establishing equilibrium. The latter condition appears to have been fulfilled in the first series of experiments and the points representing their results in Fig. 3 in general agree with those of other observers. In addition to these values Schenck, Semiller and Falcke give data concerning systems the solid phases of which they assumed to consist of iron, ferrous oxide, graphite; iron carbide ( $\text{Fe}_3\text{C}$ ), ferrous oxide, carbon (amorphous); and ferro-ferric oxide, ferrous oxide, carbon (amorphous), and Schenck and Heller<sup>14</sup> for iron, ferrous oxide, with various forms of carbon. For reasons which will appear later

<sup>13</sup> Schenck, Semiller and Falcke, *Ber.*, **40**, 1704 (1907).

<sup>14</sup> Schenck and Heller, *ibid.*, **38**, 2132, 2139 (1905).

these data and the theoretical treatment of carbide formation founded upon them are valueless.

Levin, in Nernst's *Festschrift*,<sup>15</sup> gives smoothed curves representing results by Koster in the iron: ferrous oxide and ferrous oxide: ferro-ferric oxide systems and by Van Royen in the iron: ferrous oxide system. The dotted curves of Fig. 3 are constructed from them. Experimental details have not been available to the writer and this work cannot, therefore, be criticized here. Falcke,<sup>17</sup> however, in his fourth paper (referred to below) gives a table of Van Royen's<sup>16</sup> individual results and states that they were obtained using iron treated in a stream of carbon monoxide at 600°. These experiments, therefore, parallel portions of Falcke's own work, and they are in general agreement with it.

Falcke<sup>17</sup> continuing researches begun with Schenck, experimentally proves most of the earlier work of Schenck and his co-workers to have been vitiated by the use of incompletely decomposed ferrous oxalate as a source of ferrous oxide. This preparation is indefinite, and when heated at constant temperature until gas ceases to come off, resumes evolution of carbon monoxide and dioxide upon elevation of the temperature. It was undoubtedly this partial and undefined "decomposition pressure" which was being measured by Schenck and Heller in their experiments with graphite, diamond, etc., as solid phases, since Falcke shows that under the conditions they used, no appreciable reaction is obtained with ferrous oxide and carbon. The objectionable ferrous oxalate preparation was also used in the iron—ferrous oxide—graphite, and ferro-ferric oxide—ferrous oxide—carbon experiments of Schenck, Semiller and Falcke.

The reaction between iron and carbon monoxide in the neighborhood of 600° is also studied by Falcke. He finds that carbon appears as a separate phase only when the iron is treated for a long time in a stream of the gas, as shown by the carbon residue which remains when the solid products of reaction are treated with hydrochloric acid. The products of reaction in a closed tube dissolve without residue in hydrochloric acid; in both cases hydrocarbons are formed by the treatment with acid.

Hilpert and Dieckmann<sup>18</sup> have also studied the reduction of iron oxide in a stream of carbon monoxide. Results were not very reproducible, but are generalized as follows. The products of reduction never contained oxygen. Titration with permanganate showed 99.8% of iron when

<sup>15</sup> Halle, 1912, 252.

<sup>16</sup> Van Royen, *Dissertation*, Bonn, 1911.

<sup>17</sup> Falcke, *Ber.*, 46, 743 (1913).

<sup>18</sup> Hilpert and Dieckmann, *ibid.*, 48, 1281 (1915). Other experiments on the reaction of Fe with CO are described by Gautier and Clausman, *Compt. rend.*, 151, 16, 355 (1911) and Carpenter and Smith, *J. Iron Steel Institute*, Sept., 1918. These last, for example, worked at 650° and report that the solid products contain both oxygen and carbon, and the formation of  $\text{Fe}_3\text{C}$  is indicated.

reduction occurred at  $950^{\circ}$ . At  $850^{\circ}$  the product always contained carbon and between  $720^{\circ}$  and  $800^{\circ}$  deposition of carbon by the decomposition of carbon monoxide was very greatly catalyzed. By treatment of the reduced iron with acid it was found that free carbon was not left as residue until the product attained a composition of 6% of carbon ( $\text{Fe}_3\text{C} = 6.6\%$  C). Products containing 4–6% of carbon were easily obtained, as were those containing more than 10% of total carbon. Percentages (total carbon) between 7 and 10 were not readily obtained. The Curie point in the solid masses which catalyzed the decomposition of carbon monoxide was found to be somewhat lower than that for iron carbide ( $\text{Fe}_3\text{C}$ ), which is known to be much lower than for pure iron. The authors for this reason assume unstable carbides of the type  $\text{Fe}_3\text{C}$  or  $\text{FeC}$  to have been present, and that the catalysis was due to their formation.

The results of Falcke and of Hilpert and Dieckmann make it appear certain at least that in the systems of Schenck and Heller, and Schenck, Semiller and Falcke, obtained by reaction of carbon monoxide on iron in a closed tube, carbon as a separate phase was not present, as they assumed it to be, and that if iron carbide ( $\text{Fe}_3\text{C}$ ) was ever present in large amount it should have been in the first series of experiments of Schenck, Semiller and Falcke described above.

Falcke<sup>19</sup> in another paper describes experiments with purified amorphous carbon prepared in various ways and with several varieties of purified natural graphite, compressed with iron and ferrous oxide and heated in an evacuated tube. No appreciable reaction was found to occur in any instance below  $650^{\circ}$ . Above this the different samples reacted with very different speeds. The amorphous carbon reacted very slowly and in no instance was the final equilibrium pressure observed. The graphite samples exhibited different reactivities also; pressure was developed slowly at first, then with increasing speed to a definite final value which was approximately the same in all cases. The total pressure-temperature curves fell only a little below those obtained by Schenck and Falcke and others with iron treated with carbon monoxide. Some gas analyses are also given though doubt is expressed that they necessarily represent equilibrium conditions. In only one case in all the experiments tried was there any evidence of carbide formation with the iron (*i. e.*, of hydrocarbons in the gas formed by reaction of residues with hydrochloric acid).

In a third research Falcke<sup>20</sup> obtained equilibrium data in numerous experiments involving reactions between carbon monoxide and pure iron, and iron which had been treated in a stream of carbon monoxide at  $600^{\circ}$ , (referred to as "carbonized iron") and iron, graphite and ferrous oxide.

<sup>19</sup> Falcke, *Z. Elektrochem.*, 21, 37 (1915).

<sup>20</sup> Falcke, *ibid.*, 22, 121 (1916).

The ferrous oxide was a pure preparation heated until gas was no longer evolved. It contained some higher oxides. A typical mixture as used by Falcke is 1 g. of iron, 3 g. of ferrous oxide and 0.8 g. of graphite. When iron alone was used the amount was about 3 g. The mixtures were placed in porcelain bulbs, four of which enclosed in a copper sheath could be heated simultaneously. Temperatures within the sheath were measured with a thermocouple. Because results with identical preparations deviated by amounts corresponding to  $20^\circ$ , Falcke corrected the temperatures measured with the thermocouple by utilizing the temperature coefficient of the reaction of CO upon iron. This procedure is of questionable value in the opinion of the writer. The course of reactions in which the solid phases were allowed to evolve gas starting in vacuum, or in which gas was absorbed from an initial pressure of an atmosphere, was followed by observing the total pressure. When this became constant, the gas mixtures were analyzed. Comparatively large amounts of indifferent gases were always found, and are corrected for in the final results.

The value of the equilibrium constant of Reaction 2 does not differ significantly among the different preparations in any of the experiments.

The results relating to total pressures indicate that at all temperatures the equilibrium pressure and therefore also the constant  $K = (\text{CO})^2/(\text{CO}_2)$  of the reaction



are higher for the pure iron reacting with carbon monoxide in a closed tube, than for the "carbonized" iron. When the latter preparation was heated for half an hour at  $900^\circ$ , however, new equilibrium values of the pressure were obtained at the lower temperature (without change in composition of the gas) which were close to those for pure iron. The pressures in the experiments with graphite and ferrous oxide were slightly less than with the iron treated with carbon monoxide. With graphite and ferrous oxide prepared by oxidation of iron in a stream of carbon monoxide mixed with the dioxide the pressures were still lower. The equilibrium constants of Reaction 4 as obtained from Falcke's corrected curves in the several cases are compared in Table I with those calculated from the free energies of carbon monoxide and dioxide, (referred to graphite) given by Lewis and Randall.<sup>21</sup>

TABLE I  
EQUILIBRIUM CONSTANTS,  $(\text{CO})^2/(\text{CO}_2)$

Temperature.....	600°	700°
"Pure iron".....	0.230 atm.	1.57
"Carbonized iron".....	0.148	1.27
Graphite and pure comm. FeO.....	0.115	1.18
Graphite and FeO from Fe.....	...	0.87
From free energies.....	0.080	0.965

The divergence of the results in the "pure iron" and "carbonized iron" experiments from each other and from those calculated from the free energies is seen to be larger at the lower temperature. Falcke believes

<sup>21</sup> Lewis and Randall, *THIS JOURNAL*, 37, 458 (1915).



the differences at each temperature and the approach to equality at higher temperatures to represent real effects, and suggests the formation of unstable carbides to account for them. From the analytical evidence the conclusion appears safe that carbide was present in both series, with little or no free carbon in the former, but large amounts in the latter. Just how the presence of carbide explains all the equilibrium effects is not clear to the writer. The maximum difference among the constants in Table I corresponds to about  $20^{\circ}$  in temperature, an amount which seems to be no larger than the uncertainties in the measurement and control of temperatures in the experiments. Nevertheless, Falcke later (see below) obtained similar results upon repetition of the experiments. Whatever the cause of these effects, if real, it seems assured that ferrous oxide and moderately pure iron were present as separate phases in the "carbonized iron" experiments. Whether this is true also of the "pure iron" runs cannot be said. Considerable amounts of carbon monoxide were often absorbed while the tubes were connected to the gas supply; an oxide phase may therefore have resulted. On the other hand, the ratio of carbon monoxide to iron and the side of approach do not appear to have been varied sufficiently in Falcke's experiments or those of his predecessors to prove the equilibrium to be divariant in this case. Evidence given later is strong that with small amounts of carbon monoxide tri-variant systems result. Because of this uncertainty as to the phases, no results with pure iron are finally used.

Schenck<sup>22</sup> continuing discussion of points raised by Falcke compares values of various observers of equilibrium constants of Reaction 4 in the presence and absence of iron and believes the results to be in sufficient agreement to prove the presence of carbon as a separate phase in the iron experiments. He also states that some free carbon may be observed in many cases where iron absorbs carbon monoxide, the amount depending on the duration of heating. He believes that a stable carbide is formed in part directly with carbon monoxide and in part by reaction of free carbon with iron on long heating. Discussion of the conditions for the existence of such a carbide leads him to assign the approximate formula  $\text{Fe}_7\text{C}$ .

Terres and Pongracz<sup>23</sup> have worked in the ferrous oxide:iron system and have studied the reaction of carbon dioxide upon iron.

In the equilibrium measurements, 22 g. of "Ferrum Limatum" was placed in a porcelain bulb of 146.7 cc. capacity connected with a manometer, pump and gas supply and enclosed in an electric-tube furnace. The temperature was then maintained at  $950^{\circ}$ , as measured by a thermocouple outside the bulb in the furnace, the bulb evacuated and carbon dioxide at 1 atmosphere pressure introduced. At the end of 7 hours a sample of gas was withdrawn and analyzed, the pressure being restored to 1 atmosphere by

<sup>22</sup> Schenck, *Z. Elektrochem.*, 24, 248 (1918).

<sup>23</sup> Terres and Pongracz, *ibid.*, 25, 386 (1919).

addition of more carbon dioxide. The reaction was then allowed to proceed for 16 hours longer, when a sample was again taken. The furnace was then regulated at a lower temperature, the pressure of carbon dioxide in the bulb adjusted and samples were taken after the same time intervals as before. This procedure was repeated 6 times, the temperature of the last experiments being  $550^{\circ}$ . The iron which had been used in all these runs was then treated at  $800^{\circ}$  with carbon dioxide, in the closed bulb, the gas being renewed about 40 times. The same plan was then followed with this preparation as with the iron alone, except that carbon monoxide was now used instead of the dioxide.

From the results of the gas analyses in the two series of 16-hour runs the points shown in Fig. 3 have been derived. Terres and Pongracz believed that equilibrium was actually established at  $825^{\circ}$  and above in this series because the two curves closely approach each other. (They actually cross at  $900^{\circ}$ .) They believed the larger amount of iron used to be responsible for the deviation of their results from those of other investigators and undertook to test this point.

In experiments at  $550^{\circ}$  in which powdered iron or iron wire was treated with carbon dioxide for 12 hours or a mixture of iron and iron oxide with the monoxide, it was found that increasing the weight of iron used increased the ratio of carbon monoxide to the dioxide at the end of the experiment. Since the reactions were far from completion these results do not prove anything. The same thing is true of similar experiments in which the solid phases were analyzed. Some oxide higher than ferrous was always found to be present, which the authors interpret as necessitating the assumption of solid solution of ferrous oxide and ferro-ferric oxide in one another.

In other experiments it is apparently definitely established that there is a decrease in volume when carbon dioxide reacts with iron in a closed tube. This diminution is most rapid at the beginning of the reaction and gradually falls off to zero as the reaction proceeds. If carbon monoxide and oxides of iron were the only products of the reaction this obviously would not be the case. Carbon dioxide therefore reacts directly with iron, giving carbon in some form as well as oxygen in the solid product. Apparently owing to changing "temperature coefficients of solubility" of the gases in iron, when iron is heated in a closed bulb with carbon dioxide the pressure increases as the temperature is slowly raised from  $600^{\circ}$  to  $820^{\circ}$ , decreases up to  $900^{\circ}$ , and above this increases steadily again. In a final series of experiments at  $550^{\circ}$  in which iron was treated with carbon dioxide for 12 hours, the solid and gas phases were both analyzed and a "balance" of the oxygen exchanged between them attempted. Results were not conclusive but might be interpreted as indicating a greater absorption of carbon dioxide than of the monoxide by the iron, *i. e.*, that the iron phase contained more oxygen than carbon. Criticism of the work of Terres and Pongracz will be returned to later.

Chaudron<sup>10</sup> gives equilibrium measurements obtained as follows.

Two g. of ferric oxide contained in a boat in a porcelain tube and maintained at constant temperature in a resistance furnace was treated with successive known volumes of carbon monoxide. The gas was passed in a cycle through the apparatus and over the solid oxide. The progress of the reaction was followed by means of an interferometer arranged to observe the density of the gas mixture in the system. From the known compositions of gas and the volumes used the compositions of the solid could be determined. Measurements of equilibrium composition of gas, obtained partly on reduction and partly by oxidation of the solid, were made at various temperatures. In the principal series of runs, the solid may be calculated to have consisted of approximately 50 and 75 mol % respectively of ferrous oxide with ferro-ferric oxide, and 33 and 67 mol % of iron with ferrous oxide. The results of these series, together with a few measurements in which the solid phases were prepared by oxidation of iron with carbon dioxide, are shown in Fig. 3. One point at 1050° in the ferro-ferric oxide: ferrous oxide system falls off the field of the diagram, and one of the ferrous oxide: iron points at 670° which falls very close to the curve could not be shown without obliterating several points by other observers. The temperature at which the three curves meet is given by Chaudron as 580° in his first paper and 570° in the final one.

Little criticism can be made of Chaudron's methods. The gas analyses might have been subject to minor errors due to the presence of gases other than carbon monoxide or dioxide. Other observers have often reported 2-4% of nitrogen, for example. The partial decomposition of carbon monoxide into the dioxide and carbon in the cooler zones of the furnace might also introduce uncertainties. It was found necessary to place the thermocouple outside the porcelain tube in the furnace. It is stated, however, that differences were always less than 5° in comparison tests with another couple inside the tube, after the furnace temperature had remained constant for 15 minutes. The time required for attainment of practically constant composition of gas was about 6 hours below 550° and 4 hours above. A complete circuit of the apparatus was made by the gas in about 3 hours.

Matsubara<sup>24</sup> also describes equilibrium measurements in this system.

A weighed amount of ferric oxide, prepared by ignition of purified hydroxide at a rather low temperature in a current of oxygen, was placed in a magnesia boat at the middle of a furnace in a glazed porcelain test-tube. Both ends of this tube projected beyond the furnace, the open end being connected to the vacuum, gas supply, manometer, etc. With the furnace regulated at constant temperature, a measured amount of carbon monoxide was introduced and allowed to react until equilibrium was established. The time required for this was about 2 hours at 1100° and 14 to 20 hours at 850°. (How this was determined is not stated.) The gas was then withdrawn and analyzed for carbon monoxide, carbon dioxide and nitrogen. The results of the analyses were used to calculate the composition of the solid phase. This procedure was repeated until reduction was nearly complete. The composition of the solid was checked in some instances by weighing the boat at the conclusion of an experiment and also by analysis. The compositions determined in these ways were in essential agreement. A platinum platinum-rhodium thermocouple was used for temperature measurement. The thermo-junction was outside of the porcelain tube at the center of the furnace. With both ends of the

<sup>24</sup> Matsubara, *Trans. Am. Inst. Mining Met. Eng.*, preprint No. 1051, issued with *Mining and Metallurgy*, February, 1921.

reaction tube projecting from the furnace the thermocouple could scarcely have measured accurately the temperature at any point inside the tube. Matsubara states: "correction of temperature in the furnace was made by repeating Boudouard's experiment<sup>28</sup> and by determining the composition of the gaseous phase in equilibrium with amorphous carbon at various temperatures, at nearly one atmosphere, and then determining the average temperatures in the furnace by the result of Boudouard." The magnitude of these "corrections" is not stated.

Fairly complete diagrams of equilibrium composition of gas *vs.* composition of solid phase were obtained at 1175°, 1070° and 863° respectively. That reproduced in Fig. 2 is typical. In addition, experiments were made

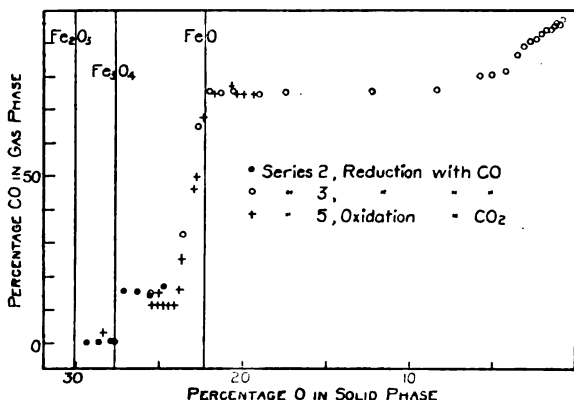


Fig. 2.—Matsubara, composition diagram at 1175° in the system Fe:C:O.

with mixtures of composition corresponding to the horizontal portions of this curve at a number of other temperatures. These results and the preceding are shown in Fig. 3. The remaining experiments and discussion in Matsubara's paper deal with the "carburization" of iron and will not be included here except to cite the results of a series of experiments at 965°.

Starting initially with about 7 g. of reduced iron containing 2.01% of oxygen, equilibrium was obtained with successive portions of carbon monoxide. In going from 2.01 to 1.43% of oxygen in the solid the equilibrium composition of gas changed from 70.72 to 75.20% of carbon monoxide and there was always an initial decrease in pressure which was then slowly regained. After this the pressure always remained lower than the initial value, the percentage of oxygen in the solid going to 0.57 and of carbon monoxide in the gas to about 91.1. Further treatment did not change the composition of the gas very much. Examination of the solid phase showed "strong carburization" but no soot deposition.

It is stated that in the last experiments of this series iron carbide or some other substance rich in carbon appeared as a separate phase, but the evidence on which this statement is based is not given. In fact the experimental evidence as to the nature of the solid phases present in this

<sup>28</sup> Boudouard, *Ann. chim. phys.*, 7, 24 (1901).

case, where Matsubara gives them as ferrous oxide dissolved in iron and iron carbide ( $\text{Fe}_3\text{C}$ ), and in other experiments in which he thinks that iron and iron carbide have been present, is very incomplete. The writer inclines to the belief that the equilibria under discussion are trivariant. However, the point is not an important one from the present standpoint.

From the data shown in Fig. 2 it may be calculated that at  $1175^\circ$  the phases which are present in the two equilibria are ferro-ferric oxide containing not more than 25 mol % of ferrous oxide, and ferrous oxide with about 12% of ferro-ferric oxide, and nearly pure ferrous oxide with iron containing about 25 mol % of dissolved ferrous oxide. This high percentage of oxygen in the iron phase is rather surprising. The points in this portion of the curve were all obtained by the action of carbon monoxide, and it is not mentioned that any special attempt was made to be sure that equilibrium had actually been reached. Further, it is possible that ferrous oxide might partly dissolve in the magnesia of the boat, which would result in curves of similar form. This behavior would have been easily observed had it occurred, but no mention of it is made. The only evidence of an experimental nature which might be brought against the solubility of ferrous oxide in iron is the claim of Schenck and Falcke that their results with carbon monoxide acting on pure iron in a closed tube could be reversed to give the same final value of equilibrium constant, together with similar experiments in the hydrogen system. This could scarcely be the case had the ferrous oxide not been present as a separate phase. Examination of these experiments does not convince the writer, however, that conditions have been varied sufficiently to prove the reactions mentioned to represent definite divariant equilibria. On the other hand the disagreement in the equilibrium constants obtained by other observers when, for example, the relative amounts of iron and gas were varied, is perhaps good evidence that Matsubara's work is correct. Pending further experiments, the writer therefore accepts the result of Matsubara that iron dissolves ferrous oxide to the extent of 20 mol % or more at the temperatures in question. This conclusion is a very important one. For example, it makes it necessary to exclude from final consideration the values of Schenck and of Falcke determined with iron and carbon monoxide in a closed tube, and of Terres and Pongracz with iron and carbon dioxide. It may be calculated from the volume of the apparatus of the last named authors that their treatment of iron with carbon dioxide did not produce enough ferrous oxide for saturation, so that even in their experiments starting with carbon monoxide, there could have been no separate ferrous oxide phase present at equilibrium. It is perhaps interesting to note that in a trivariant equilibrium of this kind, increasing the weight of iron or decreasing the volume of the gas space, other things being equal, operate in a way to make the equilibrium constant used here numerically smaller. Terres

and Pongracz were partially correct, therefore, if their reactions were completed in the time allowed, in their explanation of the lower percentages of carbon dioxide as due to the considerable weight of iron present.

Regarding Matsubara's equilibrium constants, in spite of the objectionable temperature measurement, the points lie within the limits of error upon straight lines, and appear to agree well with the average of the other determinations. They have, therefore, been given much weight in drawing the final curves.

In a fourth paper upon the subject of the reaction between ferrous oxide and carbon and between carbon dioxide and iron, Falcke<sup>26</sup> reviews the earlier work and replies to Schenck. In the review he tabulates results by Nippert<sup>27</sup> (which have not been available to the writer) in systems obtained by allowing iron to absorb carbon monoxide. He also gives results of repetitions of his own previous experiments in this system and that obtained by treatment of iron in a stream of carbon monoxide. These were accompanied by experiments in which nickel was used as catalyst in Reaction 4. The constant  $(\text{CO})^2/(\text{CO}_2)$  of this reaction is again found to be higher at all temperatures for the "pure iron" than for the carbonized, and the latter to be higher than in the nickel experiments, which are taken to be the true constants of Reaction 4. The constants of Reaction 2,  $(\text{CO}_2)/(\text{CO})$  as obtained with iron treated in a stream of carbon monoxide, are included in Fig. 3 but not distinguished from his former work. These constants again agree fairly well with those of the "pure iron" experiments, but on account of the uncertainty as to the presence of a ferrous oxide phase, neither Falcke's nor Nippert's results in this series are shown in Fig. 3. Falcke still believes that both series represent definite monovariant equilibria, and that the carbides which are present constitute the active carbon phase rather than free carbon.

### Equilibrium Constants in the System Iron : Carbon : Oxygen

In Fig. 3 the common logarithms of the equilibrium constants assumed by the different observers to correspond to the reactions



and



are plotted against the reciprocal of the absolute temperature. This procedure is adopted because of the approximately linear relationship which should hold when the variables are so chosen. Representing the partial pressures of the gases by their formulas in brackets, the equilibrium constant here used is, for each reaction,  $K = (\text{CO}_2)/(\text{CO})$ .

The only data which have been found that are not shown in Fig. 3 are

<sup>26</sup> Falcke, *Z. Elektrochem.*, **27**, 268 (1921).

<sup>27</sup> Nippert, *Dissertation*, Breslau, 1913.

those of Schenck and Heller, Schenck, Semiller and Falcke, Nippert, and Falcke in which unreduced ferrous oxalate was used, or which were obtained by the reaction of carbon monoxide upon pure iron, and the 7-hour runs of Terres and Pongracz. The 16-hour runs of the last mentioned observers are shown for comparison only; reasons have already been pointed out for rejecting them from final consideration. For all of the other points shown there is good evidence that separate, definite solid phases were present in large amounts, and the very general agreement which is found is further support of this. The points due to Falcke and to Schenck, Semiller and Falcke belong to systems in which carbon was present, obtained by deposition from carbon monoxide, or as various kinds

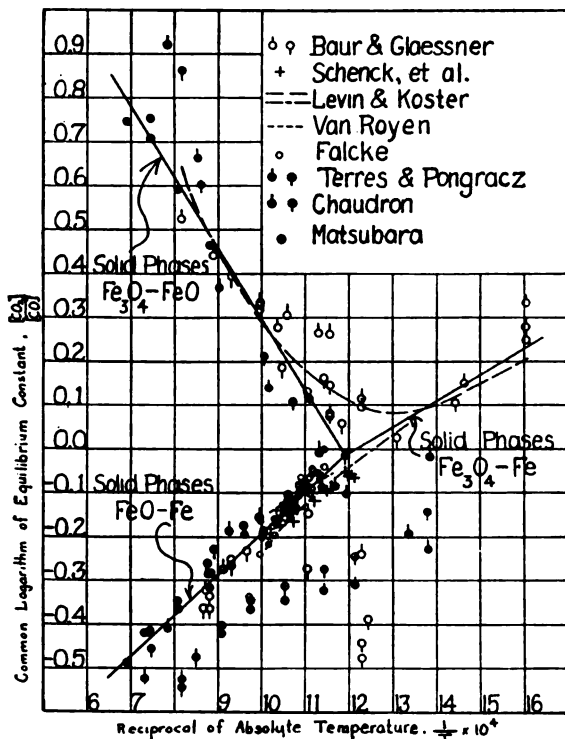


Fig. 3.—Equilibrium constants and temperature in the system Fe: C: O.

of graphite in some of Falcke's work. The points of Baer and Glaessner, Terres and Pongracz, and Chaudron are marked with a stroke pointing downward to denote that approach to equilibrium in the experiment was from the carbon dioxide side, upward for carbon monoxide.

The solid lines in Fig. 3 have been drawn as best representing all of the experiments. They conform qualitatively to the behavior required if

ferrous oxide is unstable with respect to ferro-ferric oxide and iron below  $565^{\circ}$ , the temperature at which the iron-ferrous oxide and ferro-ferric oxide—ferrous oxide curves intersect in the diagram. It is seen that the former curve is quite sharply defined: agreement in the latter case is not so good, but the general course of the curve is undoubtedly correct. At  $500^{\circ}$  and below, the points are too few and too divergent to fix the ferro-ferric oxide curve accurately, and at temperatures over  $1000^{\circ}$  some tendency to diverge is seen in the other systems also. For these reasons numerical calculations have been confined to the temperature range  $600$ – $1000^{\circ}$ . In Table II, below, are found the values of the equilibrium constants  $K_2$  and  $K_3$  of Reactions 2 and 3, respectively, as taken from the average curves of Fig. 3.

TABLE II		
EQUILIBRIUM CONSTANTS, $(\text{CO}_2)/(\text{CO})$		
Temperature $^{\circ}\text{C.}$	Fe: FeO System $K_2$	FeO: Fe <sub>3</sub> O <sub>4</sub> System $K_3$
600	0.871	1.15
700	0.678	1.77
800	0.552	2.54
900	0.466	3.43
1000	0.403	4.42

The constants in Table II refer to systems in which the solid phases are in general not quite pure. Thus in the Fe: FeO system, while the ferrous oxide phase at equilibrium is nearly pure, the iron phase probably contains considerable amounts of ferrous oxide in solid solutions, and some dissolved carbon. The fugacity of the iron in this equilibrium is, therefore, probably somewhat smaller than that of pure iron at the same temperature. The effect of this should be to make the equilibrium constant numerically larger than that for pure iron—how much larger cannot be said. The deviations of these solutions from the behavior of a perfect solution are so large and of such a character, however, that it may safely be assumed that the fugacity of the iron in these cases is essentially that of pure iron, and that the equilibrium constants,  $K_2$ , do not lie much above the true ones. In the ferro-ferric oxide:ferrous oxide system each solid phase is apparently somewhat contaminated by the other. Here the effects on the constant are partly compensating, and probably not large.

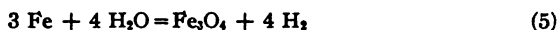
The solid curves on the diagram of Fig. 3 have been drawn for the ferrous oxide:iron and ferro-ferric oxide:ferrous oxide systems, considering only the experimental points. The intersection of these two curves together with the direct experimental points were then used to determine the ferro-ferric oxide—iron curve. In a system of this kind, however, there is a necessary connection of the three curves. Thus it can be shown that the ratio of carbon dioxide to the monoxide in the ferro-ferric oxide: iron system must be equal to  $K_2^{\frac{1}{2}} \times K_3^{\frac{1}{2}}$ . Projecting the curve



representing the latter constant linearly it is found that at  $1/T = 0.001485$ ,  $\log (\text{CO}_2)/(\text{CO})$  should be 0.065 on the ferro-ferric oxide—iron curve. The experimental curve at this point gives 0.158. Of the three the ferrous oxide—iron curve is best defined. If this kind of criterion may be used, the discrepancy of 25% represented in the above figures is due mainly to error in the ferro-ferric oxide—ferrous oxide and ferro-ferric oxide—iron curves, especially the latter, since the data relating to it are few and the experimental difficulties are greater than at higher temperatures.

### The System Iron:Hydrogen:Oxygen

In this system the very early work of Deville<sup>28</sup> is the model for all later investigations. His method of experiment was to measure the total pressure developed when water vapor from a reservoir of liquid water kept at constant temperature was allowed to react with metallic iron at a series of temperatures between 150° and 1600°. As the pressure of water vapor was its vapor pressure, it was always fixed and known, and from it and the total pressure, the pressure of hydrogen could be found. Equilibrium was regarded as established when the pressure became constant. Deville varied the weight of iron used in the different experiments, approached equilibrium from the side of increasing and decreasing pressure and, in one set of experiments, allowed hydrogen to react with large amounts of iron oxide prepared by the action of water on iron at 800°. The temperature measurement in these experiments was approximate only. Deville assumed his reactions to correspond to the equation



As has been pointed out, it is possible that in the temperature range below 500°, ferro-ferric oxide actually is the oxide in equilibrium with iron. Deville, however, had no adequate experimental ground for this assumption, and it is undoubtedly incorrect at the higher temperature.

The numerical results obtained are shown in Fig. 4 with the exception of a few at very high and very low temperatures which fall off the field of the diagram. It is seen that they are not at all concordant among themselves. Except for minor errors in the temperature scale and rather imperfect control of the water temperatures, no reason is apparent why Deville's work should not be as reliable as that of later investigators. His conditions of approach to equilibrium were more varied than in most later work, and his results probably substantiate the ideas concerning solid solution developed in the preceding, and indicate that water vapor reacting on iron in a closed tube does not produce a separate oxide phase under ordinary conditions.

<sup>28</sup> Deville, *Compt. rend.*, **70**, 1105, 1201 (1870); **71**, 30 (1871).

Preuner<sup>29</sup> in his work adopted in principle the method of Deville and also accepted without question his equation for the reaction.

In Preuner's experiments iron foil of 25 sq. cm. surface was wrapped about the porcelain thermocouple tube, and protected from it and the narrow glazed porcelain containing tube by platinum foil. The water vapor and hydrogen formed were forced back and forth through the tube between two reservoirs of water. Beginning with no hydrogen the reaction was allowed to proceed until pressure became constant. At the temperatures used, 900, 1038, and 1150°, the reaction was fast and constancy in pressure was always attained in less than 30 minutes. To get the reverse reaction, the tube was connected to the pump while being heated. This in effect subjected the iron to the action of a stream of water vapor. This treatment was carried on for 10 minutes, after which hydrogen was introduced at a pressure about twice the anticipated equilibrium pressure, and the pressure decrease observed.

The pressure-time curves so obtained from the two sides often intersected each other. This behavior Preuner attributed to the fact that the water reservoirs were often saturated with hydrogen at a pressure higher than the equilibrium value. This hydrogen would then be given off slowly, causing a gradual increase in pressure after the real equilibrium between water vapor and iron had been reached. He considers the failure of the excess hydrogen to react with oxide to restore equilibrium to be due to the very small amount of oxide and consequent slowness of reaction. When precautions were taken to exclude excess hydrogen from the water reservoirs the curves no longer crossed. The average of the values obtained beginning with water and with hydrogen were used to determine the equilibrium constant. The averages of all such determinations at the three temperatures are shown in Fig. 4. The divergence of different results at one temperature from each other is between 3 and 7%.

It is not possible to estimate independently the value of Preuner's results. In spite of his explanation of the crossing of the curves approaching equilibrium from opposite sides, this behavior casts some doubt on the validity of his results. Again, it cannot be known definitely whether or not more than one solid phase was ever present. On the other hand, his results are in good agreement with the most reliable ones which have yet appeared. The objections to his work may, therefore, be more apparent than real.

Chaudron<sup>30</sup> also uses the principle of Deville.

Two g. of iron or a mixture of 1 g. of iron and 1 g. of ferrous oxide was placed in a boat, in a porcelain tube in a resistance furnace. Temperatures of the solids were measured by a thermocouple in the tube over the boat. A few cc. only of water was used in the reservoirs at each end of the tube to establish the vapor pressure, avoiding Preuner's difficulty. Artificial circulation of gas was not used, but with the arrangement employed convection should have been vigorous. Experiments were also made in which 2 g. of

<sup>29</sup> Preuner, *Z. physik. Chem.*, **47**, 385 (1904).

<sup>30</sup> Chaudron, *Compt. rend.*, **159**, 237 (1914); *Ann. chim.*, **16**, 221 (1921).

ferrous oxide or a mixture of 1 g. of ferrous oxide with 1 g. of ferro-ferric oxide was used. The statement is made that final results were the same starting with iron or ferrous oxide alone as with the mixtures respectively. Above 400° equilibrium was attained in a few hours.

The points for the two series are shown in Fig. 4, the system in which they were obtained, but not the side of approach to equilibrium being indicated. Chaudron's curve for ferrous oxide—ferro-ferric oxide does not appear to intersect the iron—ferrous oxide curve. This undoubtedly indicates error in at least some of the points. Errors of measurement were estimated to be between 4 and 7%. Those determinations in which the mixtures of equal weights of the two solid phases were used could not well have been subject to errors due to solid solution.

Wöhler<sup>31</sup> again uses the Deville method. Like Preuner, he uses an artificial circulation of the reacting gases.

A roll of iron foil of 125 sq. cm. surface (in one case 5–10 g. of iron powder in a perforated crucible) was suspended in a vertical porcelain tube in a regulated resistance furnace. A thermocouple was inside the tube close to the iron. After establishing equilibrium by circulating the water vapor and hydrogen developed from it over the iron, the tube was evacuated, "a large amount—up to 120 cc." of hydrogen introduced and equilibrium determined with falling pressure.

The time-pressure curves obtained from the opposite sides never crossed and in some cases apparently reached almost identical values. This would ordinarily indicate a perfectly definite divariant system. It is questionable, however, whether the conditions were sufficiently varied to be assured of this in the face of the considerations previously discussed.

Schreiner and Grimnes<sup>32</sup> used the same principle as the previous investigators. They dispensed with artificial circulation of the gases and confirm their conclusion that it is unnecessary by a comparison of the times required to reach equilibrium in their experiments with those of other workers.

The iron was placed in an alundum boat in a porcelain tube connected at one end to the water container and at the other to the manometer. The thermocouple was inside the tube near the boat. The procedure was to allow the pressure to become constant starting with water vapor only. The temperature was then raised about 50°, under which condition hydrogen was used up and a constant pressure thus approached from the other side. The tube was then evacuated and equilibrium established at the last temperature beginning again with pure water vapor, and so on.

It is seen that in this research also there is no assurance at all that more than one solid phase was present. The results are again shown in Fig. 4. They are in general agreement with Wöhler but not with Chaudron, Preuner, or Deville. Of the possible reasons which the authors advance to explain this poor agreement, they seem to favor solid solution between ferrous oxide and iron.

<sup>31</sup> Wöhler, *Z. Elektrochem.*, 23, 199 (1917).

<sup>32</sup> Schreiner and Grimnes, *Z. anorg. Chem.*, 110, 311 (1920).

In his latest paper Chaudron<sup>33</sup> describes measurements intended to supplant his earlier results in the hydrogen system. He implies that with the method first used the attainment of approximate constancy of pressure is not proof of close approach to equilibrium, particularly at lower temperatures, on account of slow diffusion in the gas. Forced circulation of gas through a saturator and over the boat in the furnace was therefore resorted to in the new experiments. The solid phases were prepared in the apparatus by partial reduction of 1 g. of ferric oxide with electrolytic hydrogen. The volume of hydrogen oxidized in each preparation is given and from it the composition of the solid mixture may be calculated. In one series of measurements this corresponded to 75 mol % of ferrous oxide with 25% of ferro-ferric oxide, in another to 17 mol % of iron with 83% of ferrous oxide, and in a third to 83 mol % of iron with 17% of ferrous oxide. The last composition falls within the region where Matsubara found solid solutions. The results in this series are nevertheless in agreement with the second.

These final results of Chaudron's fall in the upper temperature range upon two curves intersecting at 570°, which is the same as the intersection point of his carbon monoxide-dioxide curves. Below 570° the points lie upon a single curve. The points shown in Fig. 4 indicate the side of approach to equilibrium, but not the particular series to which they belong. Agreement among the points is good and there is no apparent objection to the experimental work. It does not, however, agree with his earlier work. It seems unlikely that the discrepancy is due to slow gas diffusion in the first measurements, especially in view of Schreiner and Grimmes' conclusion on this point. Further, the ferrous oxide-iron curves of the first and final measurements above 600° cross at a considerable angle, rather than approach each other at the higher temperatures, as they should do if diffusion were alone responsible for the divergence.

From the values of the equilibrium constants of Reactions 2 and 6 Chaudron calculates the equilibrium constant of the water gas reaction. At 686° the constant so obtained differs from that of Haber by 40%; at 786° by 1%; at 886° by 7%; and at 986° by 5%.

### Equilibrium Constants in the System Iron:Hydrogen:Oxygen

An inspection of Fig. 4 shows the futility of any attempt to draw a curve which shall be representative of the results in the iron:ferrous oxide system. For reasons which have been discussed, there appears to be no work which can be accepted without question. That of Chaudron seems by far the most reliable, and it is possible that the average of his results will eventually be substantially verified. But until further experimental work can be done it seems that the best values of the constants in these

<sup>33</sup> Chaudron, *Ann. chim.*, 16, 221 (1921).

systems can be obtained from the carbon system. For the sake of the comparison these have been calculated, using the free energies of the iron

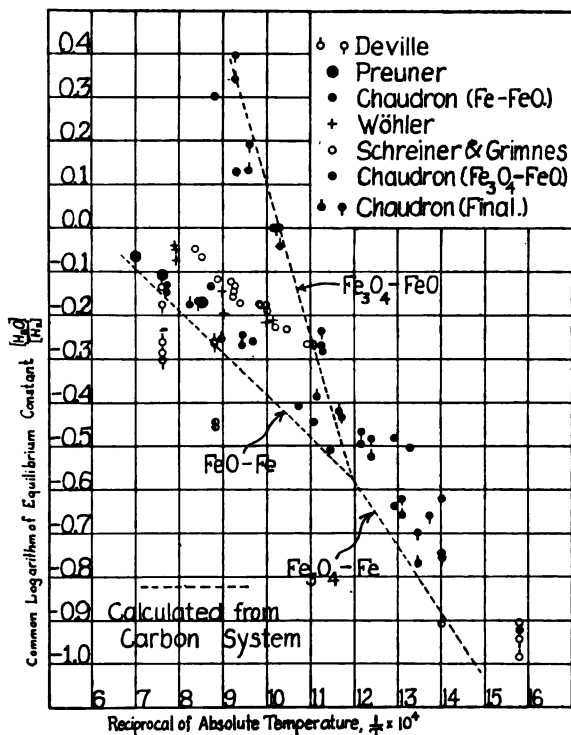


Fig. 4.—Equilibrium constants and temperature in the system Fe:H:O.

oxides as obtained from the carbon system, and the free energies of water vapor of Lewis and Randall,<sup>34</sup> and are contained in Table III below. The constants,  $(\text{H}_2\text{O})/(\text{H}_2)$  are given for the reactions



and



and are designated  $K_6$  and  $K_7$ .

TABLE III  
CALCULATED EQUILIBRIUM CONSTANTS IN THE HYDROGEN SYSTEM

Temperature °C.	Fe:FeO System $K_6$	FeO:Fe <sub>3</sub> O <sub>4</sub> System $K_7$
600	0.298	0.393
700	0.398	1.04
800	0.493	2.25
900	0.585	4.27
1000	0.662	7.2

<sup>34</sup> Lewis and Randall, THIS JOURNAL, 36, 1969 (1914).

The dotted curves of Fig. 4 represent these calculated values. With the exception of Deville's, the results of all observers lie above the calculated iron—ferrous oxide curve. Of the others the points of Preuner and Chaudron are fairly close to the curve. Deville in some cases and Chaudron in nearly all definitely had large amounts of both phases present in their determinations. Preuner may possibly have obtained a separate oxide phase in some of his experiments, though this is doubtful. These facts are perhaps of significance in connection with the better agreement with the carbon system of the points due to their work. If a separate oxide phase is not produced by water vapor acting on iron in a closed tube, the equilibrium constants obtained by the reaction should be smaller the greater the weight of iron used and the smaller the gas volume. The volume of Preuner's apparatus was undoubtedly smaller than that of any of the others, and Deville used much greater amounts of iron than the others, which may account in part for the position of their points relative to the others. It is also true that under the condition just stated the equilibrium constants with a single phase consisting of Fe with dissolved ferrous oxide should be smaller than the definitely fixed ones in the presence of a separate FeO phase. Assuming the carbon system data to be essentially correct the question then arises as to the cause of higher values generally obtained in the hydrogen system. This question cannot at present be answered. The suggestion occurs, however, that under the conditions prevailing in most of the experiments the iron surface soon gains an adherent and relatively impervious coating of oxide, the outer layers of which consist mainly of ferro-ferric oxide. Real equilibrium could then be established only by the slow diffusion of oxygen through the solid phases, which might occur extraordinarily slowly.

### The Free Energies of the Oxides of Iron

The equilibrium constants of Reaction 2, given in Table II, have been used to calculate the standard free energy changes of this reaction by means of the equation<sup>35</sup>

$$\Delta F = -RT \ln K$$

From the values of  $\Delta F$  and Lewis and Randall's<sup>34</sup> free energies of carbon monoxide and dioxide the free energies of ferrous oxide have been calculated at 100° intervals between 600° and 1000°, and are tabulated below. Using the equilibrium constants of Equation 3 (Table II) and the ferrous oxide free energies in Table IV the free energies of ferro-ferric oxide have been obtained, and are given in the table. No attempt has been made to determine theoretical equations showing free energies as functions of the temperature, as the required data do not in general exist at present. No

<sup>35</sup> The notation and conventions are those of Lewis, *THIS JOURNAL*, 35, 1 (1913).

data were found in the literature which would permit the calculation of the free energy of ferric oxide.

TABLE IV  
FREE ENERGIES OF OXIDES OF IRON

T. °C.	FeO cal.	Fe <sub>2</sub> O <sub>3</sub> cal.
600	-49700	-198320
700	-48075	-190425
800	-46445	-182550
900	-44840	-174735
1000	-43255	-166980

Without an independent check upon the results, such as would be afforded by the data in the hydrogen system if they were in agreement among themselves, the accuracy of the figures in Table IV cannot well be estimated. It is believed that the free energies of ferro-ferric oxide and ferrous oxide there given are, however, essentially correct, the latter probably to within two or three hundred calories at all temperatures.

The equilibrium constants of Table II may also be used to calculate the heat effects in Reactions 2 and 3 by means of the van't Hoff equation. Thus calculated, Reaction 2 evolves 4260 cal. and Reaction 3 absorbs 7440 cal., the temperature being the average over which the data extend, *i. e.*, about 800°. As a test of the consistency of the equilibrium data of the two reactions the heat content (heat absorbed in formation from elements) of ferrous oxide has been calculated, using the calculated heats of reactions above and the experimental heat contents of the other substances in the equations. The average of five determinations in the literature of the heat content of ferro-ferric oxide is -270200 cal. at ordinary temperatures. At 800° this becomes about -264600 cal., using specific heats of ferro-ferric oxide, iron, and oxygen as 38.9 (Regnault), 5.9 and 7.0 cal. per mol per degree and assuming them constant. From Lewis and Randall's equations the heat contents of carbon monoxide and dioxide at 800° are -26278 and -94272 respectively. Calculated from Equation 2, the heat content of ferrous oxide at 800° is then -63730 cal. and from Equation 3, -63055 cal. The difference between these results is within that which might be attributed to error in the experimental heat content of ferro-ferric oxide. Measured values of the heat content of ferrous oxide at ordinary temperatures are recorded by Le Chatelier and by Mixer of -65700 and -64300 cal., respectively.

### Summary

The present paper brings together and attempts to appraise and interpret the widely scattered and often discordant data relating to the oxides of iron and equilibria in which they are involved. The essential details of the more important researches are given. The conclusions which have

been reached in the course of this study are summarized, and the calculations which have been made are listed in the following paragraphs.

1. Ferric oxide and ferro-ferric oxide at  $1100^{\circ}$  and above form a continuous series of solid solutions, though the indications are that at temperatures much below  $1000^{\circ}$  they may not be soluble in each other in all proportions. Ferro-ferric oxide and ferrous oxide up to  $1100^{\circ}$ , at least, definitely do not form a continuous series of solutions, though they do dissolve to a limited extent in each other. Ferrous oxide appears to be soluble in iron to the extent of 20–25 mol % (6–8% oxygen) though metallic iron is not appreciably soluble in the oxide.

2. Ferrous oxide is unstable with respect to ferro-ferric oxide and iron below about  $565^{\circ}$ . Interestingly, ferro-ferric oxide shows an inversion in the same region.

3. When pure carbon monoxide reacts upon pure iron in a closed tube above  $500^{\circ}$  carbon is not ordinarily deposited as a separate phase. At temperatures above  $800^{\circ}$  a trivariant equilibrium with iron containing dissolved carbon or carbide as the solid phase may be established, or one in which the solid phase contains dissolved oxygen as well as carbon, and the gas is richer in carbon dioxide than in the former case. It is possible that stable divariant equilibria corresponding to these, with a separate dissolved carbon or carbide phase, may also be established on repeated treatment, but this does not appear to be proved. Whether monovariant systems are ever obtained, and if so what the active solid phases are, also remains to be proved.

4. With a stream of carbon monoxide acting on iron in the vicinity of  $650^{\circ}$  separate phases consisting of carbon, ferrous oxide, and iron containing dissolved oxygen and carbon (or carbide) are probably formed. At higher temperatures the oxide and separate carbon phases do not appear, and the amount of dissolved carbon decreases.

5. Carbon dioxide acting upon iron in a closed tube probably produces again a trivariant system. At temperatures in the neighborhood of  $600^{\circ}$  and lower, carbon is present in the solid phase, decreasing in amount as the temperature is increased.

6. Numerous investigators have studied univariant and divariant equilibria involving iron or ferrous oxide, ferrous oxide or ferro-ferric oxide, carbon monoxide, carbon dioxide and carbon under conditions such that the presence of separate and definite solid phases (not always quite pure) in large amounts was assured. The individual results of such investigations are graphically compared and are in sufficient agreement to permit the use of equilibrium constants and free energies based on them. These constants have been tabulated at  $100^{\circ}$  intervals between  $600^{\circ}$  and  $1000^{\circ}$  inc. Certain thermal calculations employed as checks of the equilibrium data are described.



7. Supposedly divariant equilibria involving iron or ferrous oxide, ferrous oxide or ferro-ferric oxide, water and hydrogen have been studied by only one method which in the hands of different observers yields different results. Possible reasons for these variations are discussed. It is decided that in the present state of the hydrogen system the equilibrium data cannot be used and that more reliable results may be obtained by calculation from the carbon system. Equilibrium constants so calculated are tabulated and compared graphically with the experimental ones.

BERKELEY, CALIFORNIA

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE JOHNS HOPKINS UNIVERSITY]

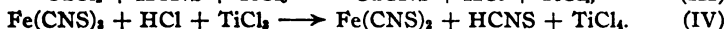
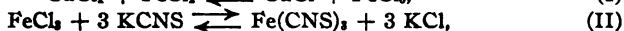
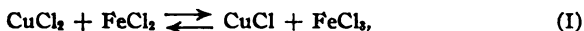
## TRIVALENT TITANIUM. II. THE ESTIMATION OF COPPER AND IRON IN THE PRESENCE OF EACH OTHER

By WILLIAM M. THORNTON, JR.

Received January 31, 1922

### Introduction

The volumetric estimation of copper through the agency of a standard solution of titanous chloride was first made known by Rhead.<sup>1</sup> The copper salt is titrated in the presence of an excess of potassium thiocyanate and a sufficient quantity of iron (all of which must be in the ferrous condition) until the red color of ferric thiocyanate just disappears. The following equations will serve to make the matter clear.



Moser,<sup>2</sup> in turn, has studied this determination and has found it possible to dispense with all indicators, relying solely upon the color of the cupric salt itself. Monnier,<sup>3</sup> however, employs certain dyestuffs, *viz.*, safranine or indulin, as indicators. Mach and Lederle<sup>4</sup> have in like manner investigated the subject. Finally, Knecht and Hibbert,<sup>5</sup> besides giving Rhead's procedure, make use of the alternate plan of adding a measured amount of standard ferric ammonium sulfate and subsequently deducting its equivalent in terms of the titanous chloride solution, the titer thus corrected being proportional to the copper only.

Regarding the determination of copper when accompanied by iron, Rhead<sup>1</sup> dismisses the case by saying that the iron may be removed as

<sup>1</sup> Rhead, *J. Chem. Soc.*, 89, 1491 (1906).

<sup>2</sup> Moser, *Chem.-Ztg.*, 36, 1126 (1912).

<sup>3</sup> Monnier, *Ann. chim. anal.*, 21, 109 (1916).

<sup>4</sup> Mach and Lederle, *Landw. Vers. Sta.*, 90, 191 (1917).

<sup>5</sup> Knecht and Hibbert, "New Reduction Methods in Volumetric Analysis," Longmans, Green and Co., 1918, pp. 13 and 55.

acetate. This cannot be taken as a felicitous suggestion; since experiments by Brearley,<sup>6</sup> which are also cited by Ibbotson,<sup>7</sup> on the separation of iron from other metals by differential hydrolysis of the acetates, go to show that of the 5 metals, manganese, zinc, cobalt, nickel and copper, the last is freed from iron with the greatest difficulty.

Knecht and Hibbert<sup>8</sup> precipitate the copper with hydrogen sulfide, and oxidize the iron in the filtrate with a mixture of ammonium hydroxide and hydrogen peroxide. After acidifying, the iron is determined by titrating with titanous chloride in the ordinary way. In a separate portion of the sample the copper and iron are estimated together. Although this process would undoubtedly yield accurate results, it has the disadvantage of being rather troublesome and lengthy.

Monnier,<sup>9</sup> however, resorts to the novel expedient of titrating one aliquot part of the test solution with titanous chloride using methylene blue as indicator, which gives the iron alone, and treating another part similarly but with either safranine or indulin as indicator, the second titer representing the sum of the copper and the iron.

In considering the above methods, it occurred to the writer that the problem of analyzing a mixture of copper and iron might be solved in an extremely simple way. If, after having titrated the two metals (in the form of their sulfates) with titanous sulfate in the presence of a soluble thiocyanate, the cuprous thiocyanate should be eliminated by filtration, then the iron could be determined in the filtrate by titration with potassium permanganate after the addition of sufficient silver nitrate to precipitate the thiocyanic acid.<sup>10</sup>

### Experimental

Known amounts of copper and iron, in the form of cupric and ferric sulfates, respectively, were taken in solution of small bulk, preferably less than 100 cc. Ten cc. of 1:1 sulfuric acid<sup>11</sup> was added and the liquid cooled with running water to 15°, whereupon, after introducing ammonium thiocyanate,<sup>12</sup> the first titration was accomplished by means of a standard solution of titanium trisulfate, the disappearance of the pink color being

<sup>6</sup> Brearley, *Chem. News*, 75, 253 (1897); 76, 49, 165, 175, 210, 222 (1897).

<sup>7</sup> Ibbotson, "The Chemical Analysis of Steel-Works' Materials," Longmans, Green and Co., 1920, pp. 7 and 90.

<sup>8</sup> Ref. 5, p. 56.

<sup>9</sup> Ref. 3, p. 113.

<sup>10</sup> Cf. Edgar, *THIS JOURNAL*, 38, 884 (1916).

<sup>11</sup> Van Name, *Am. J. Sci.*, [4] 10, 451 (1900), has shown that cuprous thiocyanate is practically insoluble in solutions containing up to 12% of conc. sulfuric acid by volume, but that precipitation is delayed when much acid is present. In the present instance it would seem that the acid concentration may vary within reasonable limits.

<sup>12</sup> From 2.5 to 5 cc. of a 10% ammonium thiocyanate solution was used depending upon the quantity of copper expected.

taken as the correct end-point. The whole was then heated to incipient ebullition to coagulate the precipitate, cooled somewhat, filtered and washed with cold water. The filtrate was cooled to 15° and the red color, which will have inevitably returned to some extent, bleached out by the very careful addition of the titanium solution (this extra portion being of course neglected). The solution was cooled still further and, after the introduction of enough silver nitrate<sup>13</sup> to precipitate all the thiocyanate, but without filtering off the precipitate of silver thiocyanate, the second titration was made with standard potassium permanganate.

The accompanying table of experimental results, wherein the relative amounts of copper and iron were greatly varied, is deemed sufficient to show that, in the main, the process has a fair claim to accuracy

TABLE I  
TEST ANALYSES

Expt.	Copper taken G.	Copper found G.	Copper error G.	Iron taken G.	Iron found G.	Iron error G.
1	0.0640	0.0634	-0.0006	0.0475	0.0478	+0.0003
2	0.1275	0.1273	-0.0002	0.0095	0.00935	-0.00015
3	0.0277	0.0280	+0.0003	0.0760	0.0760	0.0000
4	0.0259	0.0258	-0.0001	0.0665	0.0666	+0.0001
5	0.0355	0.0355	0.0000	0.0855	0.0859	+0.0004
6	0.0398	0.0403	+0.0005	0.0760	0.0760	0.0000
7	0.0120	0.0129	+0.0009	0.0950	0.0945	-0.0005
8	0.2545	0.2532	-0.0013	0.0095	0.00905	-0.00045
9	0.1590	0.1578	-0.0012	0.1399	0.1391	-0.0008
10	0.1590	0.1588	-0.0002	0.0280	0.0274	-0.0006

### Notes and Precautions

It is important to examine the titanium reagent scrupulously for iron and to apply the proper correction later when calculating the iron content of the material being analyzed. This can easily be done by the method of Newton.<sup>14</sup>

Since both end-points must be obtained in the presence of white precipitates, either of which may be of considerable magnitude, some difficulty is likely to be experienced in ascertaining the points of complete reaction. Such obstacles, however, tend to diminish with practice. In case the material to be analyzed runs very high in copper and very low in iron, it is advisable to add an accurately measured volume of standardized ferric ammonium sulfate and then deduct its value from both titrations. This will enhance the delicacy of the first color indication without reducing appreciably the exactness of the process. For sharpness of the

<sup>13</sup> A 25% solution of silver nitrate was used in conjunction with the 10% ammonium thiocyanate, volume for volume.

<sup>14</sup> Newton, *Am. J. Sci.*, [4] 25, 343 (1908).

second end-point, small volume and low temperature and good daylight are the desired conditions.

All titrations herein recorded were performed in air, the chief reason for this being that the method would thus prove more convenient in technical analysis. The small losses of trivalent titanium due to atmospheric oxidation, as noted in a previous communication,<sup>15</sup> were assumed to be approximately offset by making the standardization experiments in the air also.

### Summary

A differential volumetric process has been worked out for the estimation of both copper and iron in admixture, which depends upon the following principles.

1. The two metals, in the form of their sulfates, may be titrated in the presence of a soluble thiocyanate with a standard titanous sulfate; the titer corresponds to the sum of the copper and the iron.
2. The coagulated precipitate of cuprous thiocyanate produced in the first titration may be completely removed by filtration.
3. The small amount of ferric sulfate formed as the result of atmospheric oxidation may be reduced to the ferrous condition by the addition of an extra portion of titanous sulfate.
4. The thiocyanate may be rendered inactive toward permanganate by the introduction of silver nitrate in excess, whereupon the titration for iron may be carried out notwithstanding the presence of silver thiocyanate.
5. The titanium trisulfate must be tested for iron and the proper correction applied in case an appreciable quantity is found.

The greater part of the experimental work set forth above was executed in the laboratory of the School of Chemistry of the University of Minnesota. It is a pleasure, therefore, to thank Dean Lauder W. Jones<sup>16</sup> for encouraging the research as well as Dr. L. H. Reyerson, through whose efforts the writer enjoyed the privileges of the University of Minnesota during the summer of 1920 in the capacity of Research Fellow by Courtesy.

Moreover, the writer wishes to express his indebtedness to Mr. Frank L. LaMotte<sup>17</sup> for the gift of a liberal specimen of titanous sulfate, with which the latter part of the work was done. It was found to be virtually free from iron so that the correction previously mentioned became zero.

BALTIMORE, MARYLAND

<sup>15</sup> Thornton and Chapman, *THIS JOURNAL*, 43, 91 (1921).

<sup>16</sup> Now of Princeton University.

<sup>17</sup> LaMotte Chemical Products Company, 13 West Saratoga Street, Baltimore, Md.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF BOSTON UNIVERSITY]

## THE PHOTOCHEMICAL ACTIVITY OF THE TRIPHENYLMETHANE SULFONIC ACIDS

BY EDWARD O. HOLMES, JR.

Received February 13, 1922

### Introduction

It was accidentally discovered that Schiff's reagent contained in a clear quartz flask developed a color, apparently that of the magenta, when exposed to ultra-violet light from an iron arc. However, when the flask was removed from the light the color slowly disappeared.

At the time of its discovery, no similar reactions could be found in chemical literature but as the contents of foreign journals became available, it was seen that a reaction of the same nature had been found by Lifschitz and Joffe.<sup>1</sup> These investigators decolorized triphenylmethane dyes with potassium cyanide and brought back the color on exposure to ultra-violet light.

### Experimental

**Reaction General to Triphenylmethane Dyes.**—Attempts to reproduce this reaction with a newly prepared portion of Schiff's reagent were unsuccessful at first. However, it was soon found that the concentration of the sulfurous acid had to be very low in order that the reaction take place.

All other triphenylmethane dyes at hand were tried, consisting of malachite green, methyl violet, and crystal violet, and in each case the colorless sulfurous acid solution developed the color of the dye on exposure to ultra-violet light in a clear quartz test-tube. From these results the writer assumed that the transformation must be general to this class of dyes as the explanation of the phenomenon will show, must be the case.

**Color Developed Same as That of the Dye in Solution.**—Although to the eye the color of the dyestuff in solution and that developed by the colorless sulfurous acid solution of the dye under the influence of ultra-violet light were apparently the same, the absorption spectra of the two were compared.

**Method.**—The absorption spectrum of the dye was obtained in the usual manner by passing the light from an incandescent gas mantle through a test-tube containing a solution of the dye; and the transmitted light analyzed in a Hilger direct-reading spectroscope. However, in the case of the sulfurous acid solution of the dye, a quartz test-tube was used, and in order that the maximum color be maintained while the measurements were being made, the light from an iron arc played on the test-tube from one side.

<sup>1</sup> Lifschitz and Joffe, *Ber.*, **52B**, 1919–26 (1919); *C. A.*, **14**, 1984 (1920).

**Results.**—By this method, the bands of the dyestuff and those developed by the sulfurous acid solutions of the dye under the influence of ultra-violet light were found to be identical. In some cases the color tone was not the same to the eye. This led to the belief that there may be side reactions to a very slight extent with the formation of some other colored substances.

**Influence of Concentration of Acid on Intensity of Color Developed.**—With solutions of dye in conc. sulfurous acid no effect could be obtained. When the solution was boiled so as to reduce the concentration of the acid, the color appeared on boiling but disappeared again on cooling. This effect has already been noticed by a number of observers. However, the cooled solution was active, giving color on exposure to ultra-violet light, and as more sulfur dioxide was boiled off, it became increasingly so. This fact led to the belief that the amount of color developed might be inversely proportional to the concentration of the sulfurous acid. With this in mind, a number of quantitative measurements were made, and the results plotted in the form of curves in Fig. 1.

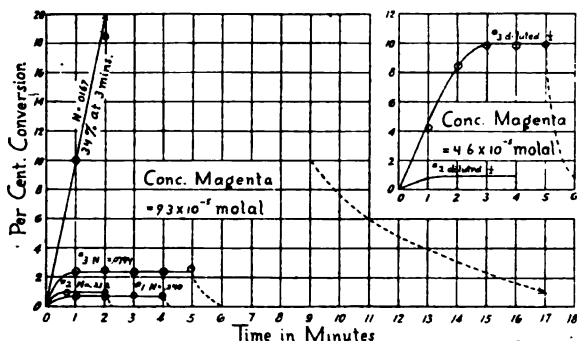


Fig. 1.—Relation of maximum color to acid concentration.

**Procedure.**—A solution of magenta of known concentration was prepared and rendered colorless by passing in sulfur dioxide. The excess of sulfur dioxide was boiled off and the strength of the residual acid determined by titration.

A portion of this solution was placed in the quartz reaction tube and exposed to the ultra-violet light from an iron arc. The amount of colored dyestuff ion formed, which is denoted in our figures by percentage conversion, was measured by comparing the color in the quartz tube with a series of standards made from the dye itself. Owing to the unevenness of the quartz tube, the color measurements could be obtained to an accuracy of only a few per cent., but this was near enough to show the shape and form of the curves. The percentage of decolorized magenta con-

verted into the colored dye was plotted along the abscissa against time along the ordinate.

Conductivity methods were not used to determine this conversion owing to the danger of photochemical effects at the electrodes of the conductivity cell. Furthermore, great inaccuracy would be introduced owing to the difficulty in measuring the very slight change in conductivity which is caused by the formation of ions from the decomposed magenta sulfonic acid (of small concentration), in the presence of such a relatively large amount of sulfurous acid.

Fig. 1 shows the curves obtained, the solid line representing the conversion into the colored form when the arc was running, and the dotted line that after the arc had been turned off.

One will notice that the smaller the concentration of the sulfurous acid, the steeper the curve and the larger the conversion. Moreover, with high concentrations of acid the color faded almost immediately, but with low concentrations it faded very slowly, sometimes taking a number of hours (not shown in the curves). Curves 2 and 3 (in insert) illustrate the results obtained when the solutions were diluted with equal amounts of water.

All the curves indicate that there is some sort of an inverse relation between the maximum color obtained and the concentration of the sulfurous acid. As the experimental error was necessarily large, the results are not good enough to determine accurately the nature of this relation.

The results up to date indicate that there are two reactions taking place: (1) a decolorizing reaction whose velocity is proportional to the concentration of the sulfurous acid or at least closely related to it; and (2) a colorizing reaction in the opposite direction whose velocity is in all probability proportional to the intensity of the ultra-violet light.

### Effect of Intensity of the Light

If the above interpretation be correct then the maximum color developed

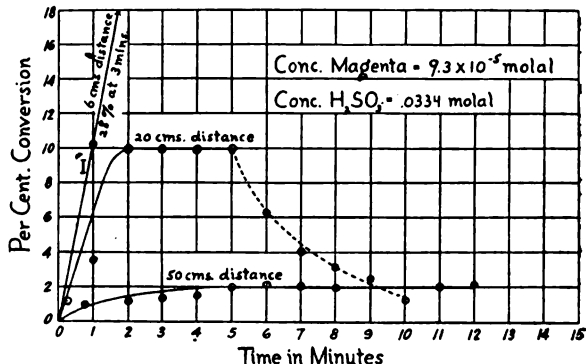


Fig. 2.—Maximum color vs. intensity of light.

should be proportional to the intensity of the light. To test this point a solution of decolorized magenta of known concentration was exposed to the rays of an iron arc at 6 cm. distance and the rate of formation of color plotted as shown in Fig. 2, Curve 1. The maximum color obtained was so intense that it was impossible by the method used in comparing colors to obtain a reading.

The solution was allowed to decolorize and then was exposed again at 20 cm. distance. The velocity was much less than in the former case and the maximum color was obtained in about 2 minutes. Again the tube was removed from the light and the color allowed to fade. It was then exposed at 50 cm. distance. The maximum color in this case was of a very low order, as can be seen from the curve.

Taking the maximum amount of color at 50 cm. distance and calculating the maximum color at 20 cm. distance, assuming that the maximum color developed is proportional to the intensity of light, we find it should be 12.5% conversion. From the curve we see that the amount actually measured is 10% which is in agreement within our experimental error. Hence the colorizing reaction must be photochemical, as its rate and the maximum color developed are proportional to the amount of light absorbed.

### Relation Between the Maximum Color and the Concentration of the Magenta

Two solutions were made up having different concentrations of magenta but the same of sulfurous acid. They were then exposed to the light until a maximum color was developed.

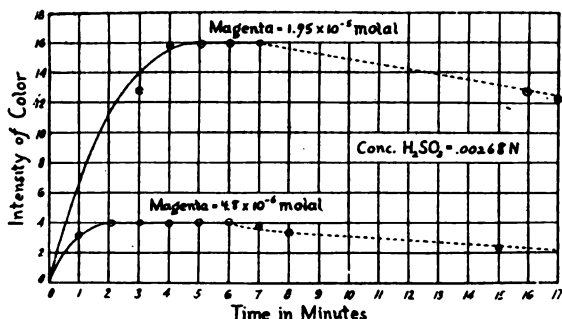


Fig. 3.—Maximum color vs. concentration of magenta at some acid concentration.

Fig. 3 shows the results in the form of two curves. The concentration of the magenta in one case was four times that in the other, and the color developed in the stronger solution was four times that in the weaker, showing a direct proportion between color and concentration of magenta.



### Maximum Color and Free Sulfurous Acid

Very remarkable results were obtained when a solution of decolorized magenta was exposed to the ultra-violet light and neutralized in steps by the addition of alkali from a buret above the reaction tube, the color being compared with a series of standards after each addition of alkali.

At certain small concentrations of sulfurous acid a maximum color was obtained instead of at the neutral point, as would be expected. After passing the maximum point, the color faded rapidly, and when the solution was neutral the color had entirely disappeared. By adding acid in the same fashion the curve could be retraced, and could be reproduced at will from either the acid or the alkaline side. Fig. 4 shows the curves ob-

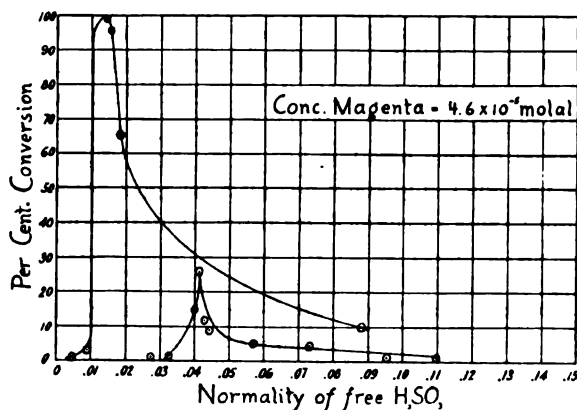


Fig. 4.—Maximum color vs. free sulfurous acid.

tained, each curve representing the same solution of magenta but having different concentrations of sulfurous acid originally present. These results can be satisfactorily explained only after further investigation.

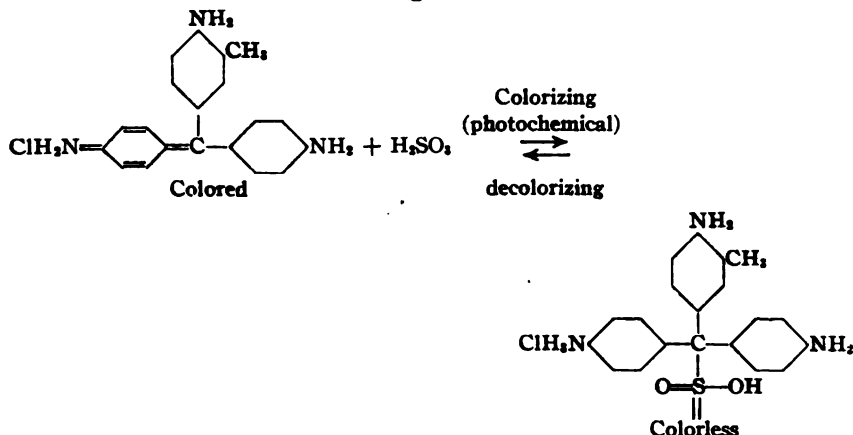
### Mechanism of the Reaction

Although the measurements were necessarily only good approximations, they leave no doubt that there are two reactions concerned in the phenomenon: (1) the decolorizing reaction taking place between the magenta and the sulfurous acid; and (2) a colorizing reaction decomposing the product formed by the first reaction which must be of a photochemical nature.

According to Hantzsch<sup>2</sup> the reaction between magenta and sulfurous acid is not a case of reduction but the formation of an addition product causing a breaking of the quinoid structure and hence the disappearance of color. A sulfonic acid is formed which is quite stable at ordinary

<sup>2</sup> Hantzsch, *Ber.*, **33**, 289 (1900).

temperatures and has been isolated and analyzed. A structural representation of the two reactions is given below.



At ordinary temperatures and in daylight the point of equilibrium is far to the right as the solution is colorless. Hence the velocity of decomposition of the sulfonic acid under these conditions must be very small. However, under the influence of ultra-violet light this velocity is greatly increased, and the equilibrium is shifted towards the left, the solution becoming highly colored. The extent to which the equilibrium is shifted depends on the already mentioned factors.

This same equilibrium can also be shifted by other means. If a solution of the colorless sulfonic acid is heated, the color of the dye appears but subsequently disappears again on cooling, the reason for this being the difference in temperature coefficients of the two reactions. Moreover, by the addition of alkali the color can be made to appear as the sulfurous acid is used in neutralization and the equilibrium caused to shift to the left.

An expression for the equilibrium constant might be derived by the aid of either the Byk or the Weigert theory of photo-stationary states but as these theories are at variance in certain particulars, such an expression was not attempted. However, by making certain assumptions a simple expression can be derived the value of which remains to be determined by experiment.

**Ultra-violet Light and Heat.**—The shifting of the equilibrium which takes place at high temperatures has been caused to occur at room temperature under the influence of ultra-violet light. In terms of the quantum theory, the large quanta causing the reaction to take place are supplied by the high frequency of the ultra-violet light and added to those already present in the system, thereby increasing the radiation density and causing an increase in reaction velocity, dependent thereon. The ultra-violet light acts as "cold heat," so to speak.

**Wave Length of Light Causing the Reaction.**—There was no appa-

ratus available for the measurement of the active wave lengths causing the reaction, but inasmuch as the reaction does not take place in glass which is opaque below 3300 Å. U. and does take place in the light of an iron arc which emits nothing below 2200 Å. U., the active rays lie between these limits.

### Summary

1. Schiff's reagent was found to give a red color under the influence of ultra-violet light upon exposure in a clear quartz tube.

2. Other triphenylmethane dyes that had been decolorized by sulfur dioxide, forming sulfonic acids, gave their characteristic colors under similar circumstances.

3. The color developed in each case was proved to be that of the dye itself.

4. It was shown that there were two reactions taking place: (1) a decolorizing reaction; and (2) a coloring reaction which is photochemical.

5. The large quanta supplied by the ultra-violet light cause the velocity of the photochemical reaction to increase; hence a shifting of the equilibrium takes place.

6. The equilibrium in this system can be shifted by chemical and thermal as well as photochemical means.

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BOSTON, MASSACHUSETTS

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

## A REVISION OF THE ENTROPIES OF THE ELEMENTS

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In the future development of thermodynamic chemistry it is probable that some of the greatest advances will be made through two new thermodynamic principles.

The first of these is known as the Third Law of Thermodynamics, which, when stated with proper caution,<sup>1</sup> may now be regarded as one of the exact laws of nature. Such doubt as may have existed regarding the adequacy of its experimental verification we believe will be resolved by the further and more precise evidence which is to be adduced in the present article.

<sup>1</sup> See Lewis and Gibson, "The Third Law of Thermodynamics and the Entropy of Solutions and of Liquids," [THIS JOURNAL, 42, 1529 (1920)]. A more complete statement of the third law is given by Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill, New York (in press).

The other principle which we are about to discuss, and which concerns the entropy of monatomic gases, has an equal claim to consideration as an exact law of nature.

In chemical calculations based upon these principles, the entropies of the elements will play so large a part that they doubtless will become recognized as among the most important of all physico-chemical constants. Since the publication of the first table of the entropies of the elements<sup>2</sup> new data and new methods have become available which warrant a revision of that table.

### The Entropy of Monatomic Gases

The entropy of a perfect gas, whose molal heat capacity at constant volume is  $3/2R$ , is given by the familiar expression

$$S = 3/2 R \ln T + R \ln V + \text{const.} \quad (1)$$

In the classical theory of thermodynamics no attempt was made to evaluate this constant which might, at will, have been assigned any finite or infinite value, positive or negative. However, since the adoption of Planck's suggestion to take the entropy of a certain class of substances as zero at the absolute zero of temperature, it has become possible to state the numerical value for the entropy of a substance in a given state. It therefore became a matter of interest to evaluate the constant in Equation 1 for various monatomic gases.

Sackur<sup>3</sup> in such an investigation found that by adding a new term to the entropy equation, namely,  $3/2R \ln W$ , where  $W$  is the molecular weight of the gas, the residual constant is the same for different gases. Thus,

$$S = 3/2 R \ln T + R \ln V + 3/2 R \ln W + C \quad (2)$$

and  $C$  is independent of the nature of the gas.

This generalization, which at the time of its discovery could only roughly be verified, has stood the test furnished by the far more accurate and extensive determinations of entropy which have since been made.<sup>4</sup> On the other hand, the numerical value of the constant  $C$  which Sackur calculated from certain speculations relating to the quantum theory, has not been corroborated; although a similar calculation of Tetrode<sup>5</sup> comes nearer to the experimental value.

It has, however, recently been shown by Lewis<sup>6</sup> that the constant  $C$

<sup>2</sup> Lewis and Gibson, *THIS JOURNAL*, 39, 2554 (1917).

<sup>3</sup> Sackur, *Ann. Physik*, 36, 598 (1911); 40, 67 (1913).

<sup>4</sup> See the paper by Tolman [*THIS JOURNAL*, 42, 1185 (1920)] who obtained values for the entropies of numerous monatomic gases, with the aid of our previous entropy tables.

<sup>5</sup> Tetrode, *Ann. Physik*, 38, 434 (1912).

<sup>6</sup> Lewis, *Phys. Rev.*, 18, 121 (1921). This question is discussed more fully in the volume dedicated to Professor E. H. Hall; "Contributions from the Jefferson Physical Laboratory," Vol. 15, Cambridge, Mass.

can be calculated, with an accuracy far greater than can yet be attained by experiment, from other well known constants of nature. This calculation, which depends upon the theory of ultimate rational units,<sup>7</sup> may be best presented by writing Equation 2 in the equivalent forms,

$$S = R \ln (T^{3/2} W^{1/2} V) + C \quad (3)$$

$$S = R \ln (C' T^{3/2} W^{1/2} V) \quad (4)$$

where  $R \ln C' = C$ .

Now, according to this theory of ultimate rational units,  $C'$  and  $C$  become unity and zero respectively when for  $W$  and  $V$  we substitute the mass of one molecule and the volume per molecule, and when mass, volume and temperature are expressed in the new units. For conversion we have the relation that 1 erg-cm. becomes  $1/(4\pi e)^2$  in ultimate rational units (U.R.U.). Here  $e$  is the charge of an electron in ordinary electrostatic units, namely,  $4.774 \times 10^{-10}$ .

We thus find

$$C' = \frac{k^{3/2} c^3}{N^{1/2} (4\pi e)^2} = 3.252 \times 10^{-3} \quad (5)$$

where  $k$  is the gas constant for one molecule,  $1.372 \times 10^{-16}$ ;  $c$  is the velocity of light,  $2.999 \times 10^{10}$ , and  $N$  is the number of molecules in a mol,  $6.059 \times 10^{23}$ . From these values we find that in ordinary units  $C = R \ln C' = -11.39$ . Because of possible errors in the constants employed, this value is in doubt by about 0.01 unit. Equation 3 then becomes

$$S = R \ln (T^{3/2} W^{1/2} V) - 11.39. \quad (6)$$

Thus with the aid of these fundamental constants, the electron charge, the gas constant, Avogadro's constant, and the velocity of light, and with no further experimental information, we are able to calculate the entropy of any gas of known molecular weight, which obeys the perfect gas law, and which has the heat capacity characteristic of monatomic gases.

For tabulating entropies at 25° and 1 atmosphere, we may substitute for the temperature and volume (the latter from the gas law) and thus find for these conditions

$$S = 3/2 R \ln W + 25.70. \quad (7)$$

For only 4 monatomic gases have we experimental determinations of the entropy of sufficient accuracy to justify comparison with the theo-

TABLE I  
ENTROPY OF FOUR MONATOMIC GASES AT 25° AND 1 ATMOSPHERE

	By expt.	Calc.		By expt.	Calc.
He.....	29.2	29.8	Cd.....	40.0	39.8
A.....	36.4	36.7	Hg.....	41.3	41.5

retical equation. Table I shows the remarkable agreement between the values calculated by Equation 7 and the experimental values in these

<sup>7</sup> Lewis and Adams, *Phys. Rev.*, 3, 92 (1914).

4 cases, the difference in no case exceeding the probable experimental error.

For helium and argon the experimental values are those given in the table of Lewis and Gibson. From the value for liquid mercury, given in that table, we have obtained the value for mercury vapor by adding the entropy change in vaporization as calculated from the very accurate vapor pressure measurements of Smith and Menzies,<sup>8</sup> and of Menzies.<sup>9</sup> From the formula which they give we may calculate immediately the entropy change in passing from liquid to gas, both at one atmosphere, and at  $25^{\circ}=298.1^{\circ}$  K. We find  $\Delta S=23.50$ , which, added to the entropy of liquid mercury, 17.80, gives the entropy of mercury vapor at this temperature and pressure, namely  $S_{298}=41.30$ .

For the entropy of vaporization of cadmium we have used the value calculated by Tolman from the vapor pressure measurements of Egerton,<sup>10</sup> namely,  $\Delta S_{298}=28.2$ . Adding this to the value 11.8 which we are going to obtain for the entropy of solid cadmium from the measurements of Griffiths, we find for the vapor,  $S_{298}=40.0$ .

We see, therefore, that the principle of Sackur, combined with the principle of ultimate rational units, leads to values of the entropy which agree with the experimental values within the limits of experimental error. The four gases which we have available for this comparison range in atomic weights from 4 to 200. Moreover, it has recently been shown by Tolman<sup>11</sup> that, at least in order of magnitude, the same equation is valid for free electrons with atomic weight 0.000544.

### General Considerations Relating to the Entropy of Solids and of Diatomic Gases

It has been shown by Latimer<sup>12</sup> that also in the case of solids the atomic weight is the chief factor in determining the entropy. Indeed, by assuming it to be the sole factor, and using an equation similar in form to Equation 7, but with a different constant, he obtained values for the entropies of a large number of solids which agreed very closely with those obtained experimentally. In one or two cases, to which we shall allude later, he was able in this way to discover errors in the experimental data (or their interpretation) which entered into the table of Lewis and Gibson; such conclusions being later confirmed by new experiments or by re-inspection of the older data.

Nevertheless, such calculations as these cannot be completely valid, for the entropy of any substance must vary not only with the temperature but also with the volume, and if any completely general law can be obtained for the entropy of solids it must be one which involves not only atomic weight and temperature but also some quantity such as the atomic volume, or the constraint operating on the atoms of the solid. Evidently, however, the term due to such factors is either small or approximately

<sup>8</sup> Smith and Menzies, *THIS JOURNAL*, 32, 1434 (1910).

<sup>9</sup> Menzies, *ibid.*, 41, 1783 (1919).

<sup>10</sup> Egerton, *Phil. Mag.*, 33, 333 (1917).

<sup>11</sup> Tolman, *THIS JOURNAL*, 43, 1592 (1921).

<sup>12</sup> Latimer, *ibid.*, 43, 818 (1921).

constant in the salts, which Latimer employed chiefly, and his principle will be of much service is estimating the entropies of solid substances when exact experimental data are lacking.

Similar remarks may be made with regard to Latimer's calculation of the entropy of diatomic gases, where only the atomic weights are considered and not the constraints between the atoms. Here, also, the mass appears to be the predominant factor and the method is capable of predicting the approximate entropies of substances of this class, usually within one or two entropy units.

### New Determinations of Atomic Entropies of Metals

**Sodium.**—Recent investigations by Griffiths and Griffiths,<sup>13</sup> and by Günther,<sup>14</sup> on the specific heat of metallic sodium are in accord with the data of Eastman and Rodebush<sup>15</sup> which were used in the former table of Lewis and Gibson. Unfortunately the new work goes to no lower temperature. There is no change to be made in the former value for the entropy of sodium.

**Potassium.**—In the former calculation of the entropy of potassium, entire weight was given to the old calorimetric values for the heat of formation of potassium salts. In spite of the fact that the specific-heat measurements have not been carried to sufficiently low temperature to determine with any precision the value of  $\Theta$  (the temperature at which  $C_p = 3/2 R$ ), the results of Eastman and Rodebush show that no great error would be made by assuming  $\log \Theta = 1.32$ . Using this value and the graphical method of Lewis and Gibson we find for potassium  $S_{298} = 16.6$ .

**Calcium.**—Günther has investigated the heat capacity of calcium at lower temperatures than those employed by Eastman and Rodebush. His results fall very near to the curve formerly adopted, but a curve drawn through the points of both series leads to a slightly lower value for the entropy. In place of the former value, 11.0, we now find  $S_{298} = 10.64$ .

**Aluminum.**—The new data of Griffiths and Griffiths permit a slight improvement in the heat capacity of aluminum in the neighborhood of room temperature. In place of the former value of 6.9 we thence obtain  $S_{298} = 6.82$ .

**Iron.**—The former value for the entropy of iron based solely on the measurement of Dewar, was  $S_{298} = 6.6$ . The data of Günther at low temperatures and of Griffiths and Griffiths at higher temperatures do not fall upon quite the same curve, the specific heats of the former investigation being lower. It is probable that in the case of a metal like iron the specific heat will be found to vary appreciably with the previous mechanical

<sup>13</sup> Griffiths and Griffiths, *Proc. Roy. Soc. (London)*, 90A, 557 (1914).

<sup>14</sup> Günther, *Ann. Physik*, [4] 63, 476 (1920).

<sup>15</sup> Eastman and Rodebush, *This Journal*, 40, 480 (1918).

and thermal treatment of the metal. Nevertheless, it is to be noted that in general the specific heats obtained by Günther are a little low. We have given a little more weight to the measurements of Griffiths and Griffiths and thus find  $\log \Theta = 2.016$ , and  $S_{298} = 6.71$ .

**Zinc.**—The measurements of Griffiths and Griffiths lead to no appreciable change in the entropy. Instead of the former value 9.8 we find  $S_{298} = 9.83$ .

**Cadmium.**—Previously the only measurement which could be used for determining the entropy of cadmium was the one by Dewar which led to the value  $S_{298} = 11.6$ . The data of Griffiths and Griffiths lead to a slightly higher value, namely,  $S_{298} = 11.80$ .

**Copper.**—The specific heat of copper has been more fully investigated than that of any other substance. The newer work of Kamerlingh Onnes<sup>16</sup> confirms previous experiments at low temperatures. The work of Griffiths and Griffiths at higher temperatures leads to a greater precision of the curve in the range where  $C_p - C_v$  is appreciable. In place of the old value 8.0 we find  $S_{298} = 8.18$ .

**Silver.**—Here also the measurements of Griffiths and Griffiths lead to an insignificant change, and  $S_{298} = 10.25$ .

**Lead.**—Once more using the data of Griffiths and Griffiths, the entropy of lead is raised from 15.4 to  $S_{298} = 15.53$ .

**Tin.**—Between ordinary white tin and the gray tin which is stable below  $19^\circ$  the difference in entropy can be calculated from the measurements by Brönsted<sup>17</sup> of the transition temperature and heat of transition. We thus find that at  $25^\circ$  the entropy of the white tin is greater by 1.87.

Brönsted has also measured the specific heats of the two forms at low temperatures, and from his measurements we find, by the graphical method of Lewis and Gibson; for white tin,  $\log \Theta = 1.688$ , and  $S_{298} = 11.17$ ; while for gray tin  $\log \Theta = 1.800$ , and  $S_{298} = 9.23$ . The difference in entropies is 1.94 and the agreement between this value and the value 1.87 found above furnishes a remarkable confirmation of the third law.

### Further Tests of the Third Law, and the Entropy of Some Non-Metals

**The Chlorides of Some Heavy Metals.**—In the paper of Lewis and Gibson six independent values of the entropy of chlorine were obtained, but with an average deviation from the mean of nearly 2 entropy units. Four of these values were obtained from the free energy and heat of formation of the chlorides of mercury, lead, silver and thallium. The probable errors in the calorimetric measurements of the heats of reaction were alone considered sufficient to account for the discrepancies.

In an investigation which is not yet entirely completed, Mr. R. H.

<sup>16</sup> Kamerlingh Onnes, *Comm. Phys. Lab. Leiden*, No. 147 (1915).

<sup>17</sup> Brönsted, *Z. physik. Chem.*, 88, 479 (1914).



Gerke has obtained the electromotive force and the change in electromotive force with temperature for three cells, namely,

(a)  $\text{Ag}, \text{AgCl}, {}^{18}\text{HgCl}, \text{Hg}; E_{298} = 0.0455; dE/dT = 0.000338$

(b)  $\text{Pb}, \text{PbCl}_2, \text{AgCl}, \text{Ag}; E_{298} = 0.4901; dE/dT = -0.000186$

(c)  $\text{Tl}, \text{TlCl}, \text{AgCl}, \text{Ag}; E_{298} = 0.7788; dE/dT = -0.000048.$

In each case the electrolyte was molal potassium chloride or hydrochloric acid.

Now the entropy change, in each cell reaction, is very simply obtained by multiplying  $dE/dT$  by 23074, which is the factor that converts volt equivalents into calories. On the other hand, the same change in entropy may be calculated from the entropies of the metals and their chlorides, as obtained from specific heats, in this paper and in that of Lewis and Gibson. The values of  $\Delta S$ , obtained by the two methods, are compared in Table II.

TABLE II

Reaction	$\Delta S(\text{e.m.f.})$	$\Delta S(\text{sp. heats})$
(a) $\text{Ag} + \text{HgCl} = \text{AgCl} + \text{Hg} \dots \dots \dots$	7.8	7.7
(b) $\frac{1}{2}\text{Pb} + \text{AgCl} = \frac{1}{2}\text{PbCl}_2 + \text{Ag} \dots \dots \dots$	-4.3	-4.3
(c) $\text{Tl} + \text{AgCl} = \text{TlCl} + \text{Ag} \dots \dots \dots$	-1.1	0.9

It is evident in the case of the chlorides of silver, mercury and lead that the former apparent deviations from the third law, amounting to several entropy units, are now completely eliminated.<sup>19</sup> In the third reaction there is a discrepancy of two entropy units, but a re-inspection of the specific-heat data of thallous chloride shows that the value of the entropy obtained by Lewis and Gibson is unquestionably too high.

However, even if we give full value to the entropy of thallous chloride as formerly calculated, *the average apparent deviation from the third law in the case of these chlorides has been reduced tenfold.*

**The Entropy of Chlorine.**—Gerke has also studied the cell with chlorine and silver—silver chloride electrodes in molal hydrochloric acid. His present results give<sup>20</sup>  $E_{298} = 1.1360, dE/dT = -0.00057$ . Hence we find,  $\text{Ag} + \frac{1}{2}\text{Cl}_2 = \text{AgCl}; \Delta S_{298} = -13.15$ . Lewis and Gibson found for  $\text{AgCl}, S_{298} = 23.4$ ; and we have found for  $\text{Ag}, S_{298} = 10.25$ . Hence we find for  $\frac{1}{2}\text{Cl}_2, S_{298} = 26.3$ . The same value would have been obtained by combining the e.m.f. and specific-heat data involving the other chlorides except that of thallium.

<sup>19</sup> The silver chloride here used is that prepared by adding a chloride to a silver salt in aqueous solution. It is, therefore, presumably the same as that employed in the specific-heat measurements.

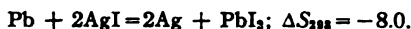
<sup>20</sup> The exactness of the agreement between the two values of  $\Delta S$  obtained in Reactions (a) and (b) must be somewhat fortuitous, since the data on the heat capacities of the chlorides do not permit great precision in the estimation of their entropies.

<sup>20</sup> These values combined with those for Cell (a) give the heat of formation of  $\text{HgCl}$  as 31400 cal., which is very close to the value 31500 as obtained by Nernst [*Z. physik. Chem.*, 2, 23 (1888)], and by Varet [*Ann. chim. phys.*, [7] 8, 102 (1896)].

**Iodine.**—In the former table the atomic entropy of iodine was given as 15.7. This value was based on specific heat measurements of Nernst. The more recent experiments of Günther<sup>21</sup> showed that both his own measurements and those of Nernst were affected by some peculiar phenomenon which he believed to be a slow transition between two forms of iodine. It seems at present impossible to obtain any reliable value for the entropy of iodine from the specific heats.

However, we may determine the entropy through the third law by means of a measurement by Gerke of the temperature coefficient of the electromotive force of the cell  $\text{Pb, PbI}_2, \text{Pb(ClO}_4)_2, \text{PbI}_2, \text{I}_2 (\text{solid})$ . He thus finds for the reaction  $\text{Pb} + \text{I}_2 = \text{PbI}_2$ ;  $\Delta S_{298} = -1.20$ .

The entropy of lead iodide as obtained by Lewis and Gibson from specific-heat measurements was 41.3; we may obtain another value by using their entropy of silver iodide, our value for silver, and Gerke's measurement,



Whence for  $\text{PbI}_2$ ,  $S_{298} = 40.6$ . We may take the average value for  $\text{PbI}_2$ , namely,  $S_{298} = 41.0$ .

We have found the entropy of lead to be 15.5, and combining these values with Gerke's value for the entropy of formation of lead iodide from lead and iodine, we find for  $\text{I}_2(\text{s})$ ,  $S_{298} = 26.6$ , and therefore for  $\frac{1}{2}\text{I}_2(\text{s})$ ,  $S_{298} = 13.3$ .

The heat of sublimation of iodine has been carefully measured by Baxter, Hickey and Holmes,<sup>22</sup> from whose work we find  $\Delta H_{298} = 15100$ . Also from their vapor-pressure measurements we may calculate the free energy change,  $\Delta F_{298} = 4630$ . Hence  $\Delta S_{298} = 35.2$ , and combining this with the value for solid iodine we obtain for  $\frac{1}{2}\text{I}_2(\text{g})$ ,  $S_{298} = 30.9$ .

**Bromine.**—The former value for the entropy of bromine was obtained from very meagre specific-heat data largely by analogy to iodine and chlorine. Since our new values for these elements are lower than those obtained from the specific heats, that for bromine presumably should be lowered by a corresponding amount. As a very rough estimate we shall therefore take for  $\frac{1}{2}\text{Br}_2(\text{l})$ ,  $S_{298} = 16.3$ .

In this case, also, we may obtain the entropy change in vaporization from vapor-pressure measurements. Using the data of Ramsay and Young<sup>23</sup> we find for  $\frac{1}{2}\text{Br}_2(\text{g})$ ,  $S_{298} = 27.7$ .

**Oxygen.**—In the case of oxygen we have three independent methods of determining the entropy, which afford a very good test of the third law. From the measurements of Eucken of the specific heats and heats of transi-

<sup>21</sup> Günther, *Ann. Physik*, [4] 51, 828 (1916).

<sup>22</sup> Baxter, Hickey and Holmes, *This Journal*, 29, 127 (1907).

<sup>23</sup> Ramsay and Young, *J. Chem. Soc.*, 49, 453 (1886).

tion of the various forms of oxygen, Lewis and Gibson found for  $\frac{1}{2}\text{O}_2$ ,  $S_{298} = 24.1$ .

They also show how it is possible from the entropy of graphite and of carbon monoxide, and from the heat and the free energy change in the formation of carbon monoxide from carbon and oxygen, to calculate the entropy of oxygen. Hence for  $\frac{1}{2}\text{O}_2$ ,  $S_{298} = 22.8$ .

A third very reliable calculation is now permitted by the measurements of Günther<sup>21</sup> on the specific heat of mercuric oxide. From his data we find by the usual graphical methods for  $\text{HgO}$ ,  $S_{298} = 16.3$ . From the heat of formation and free energy of formation of mercuric oxide, as obtained from various data by Lewis and Randall,<sup>24</sup> we find the entropy change in the formation of mercuric oxide from its elements, namely,  $\Delta S_{298} = 26.1$ . The entropy of mercury from the former table is 17.8, and by combining these several data, we find for  $\frac{1}{2}\text{O}_2$ ,  $S_{298} = 24.6$ .

These three values, 24.1, 22.8 and 24.6 certainly agree within the limits of experimental error of the three methods, and we may finally take, as a weighted mean, 24.0.

**Nitrogen.**—New work by Kamerlingh Onnes<sup>25</sup> on the specific heat of solid and liquid nitrogen confirms in a most satisfactory manner the work of Eucken, and leads to no change in the value of the entropy of this element.

**Hydrogen.**—An entirely new method of determining the entropy of hydrogen is furnished by Equation 6, for Eucken has shown that below about 60° K hydrogen has the heat capacity of a monatomic gas, and under these conditions there can be little doubt that its entropy can be calculated as for a monatomic gas of atomic weight 2.<sup>26</sup> We may therefore calculate its entropy, say at the boiling point of liquid hydrogen, and then use the data of Eucken, as in the paper of Lewis and Gibson, to find the entropy at 25°. This gives us for  $\frac{1}{2}\text{H}_2$ ,  $S_{298} = 14.72$ . This is more certain than any other determination of the entropy, and we may take it as the final value. Lewis and Gibson obtained 15.9 from the specific heat of ice and the third law, while they obtained 14.7 from the specific heat of hydrogen. In the meantime, however, Kamerlingh Onnes<sup>27</sup> has redetermined the heat of fusion of solid hydrogen, the specific heat of liquid hydrogen, and the vapor pressure of the latter, at several temperatures, whence we may obtain the entropy of vaporization; and these data lead to a value for the entropy of hydrogen which is 0.67 higher than the value which we have just obtained from the principle of ultimate rational units through Equation 6. But it is to be noted that this discrepancy

<sup>24</sup> Lewis and Randall, *THIS JOURNAL*, **36**, 1969 (1914).

<sup>25</sup> Kamerlingh Onnes, *Comm. Phys. Lab. Leiden*, **149** (1916).

<sup>26</sup> See Tolman, *THIS JOURNAL*, **42**, 1185 (1920).

<sup>27</sup> Kamerlingh Onnes, *Comm. Phys. Lab. Leiden*, **153** (1917).

is no greater than the uncertainty which probably still exists in the heat of vaporization and the heat of fusion of hydrogen.

### Summary

In Table III we shall collect for reference all of the atomic entropies which have been so far calculated, also including the entropies of a number of elements in the state of monatomic gas, as calculated from Equation 7.

TABLE III  
ATOMIC ENTROPIES AT ONE ATMOSPHERE AND 25°

	$S_{298}$		$S_{298}$
Electricity ( $E^-$ , g).....	3.28	Copper.....	8.18
Hydrogen ( $\frac{1}{2} H_2$ ).....	14.72	Zinc.....	9.83
Hydrogen (H).....	25.72	Zinc (g).....	38.17
Helium.....	29.83	Bromine ( $\frac{1}{2} Br_2$ , l).....	16.3
Lithium.....	7.6	Bromine ( $\frac{1}{2} Br_2$ , g).....	27.7
Lithium (g).....	31.48	Bromine (Br, g).....	38.77
Beryllium.....	7.3	Krypton.....	38.88
Carbon (diamond).....	0.6	Rubidium (g).....	38.97
Carbon (graphite).....	1.3	Zirconium.....	9.5
Nitrogen ( $\frac{1}{2} N_2$ ).....	22.8	Molybdenum.....	7.5
Nitrogen (N).....	33.57	Ruthenium.....	6.9
Oxygen ( $\frac{1}{2} O_2$ ).....	24.0	Rhodium.....	7.6
Oxygen (O).....	33.97	Palladium.....	8.9
Fluorine (F).....	34.48	Silver.....	10.25
Neon.....	34.66	Cadmium.....	11.80
Sodium.....	12.2	Cadmium (g).....	39.79
Sodium (g).....	35.06	Tin (white).....	11.17
Magnesium.....	8.3	Tin (gray).....	9.23
Aluminum.....	6.82	Iodine ( $\frac{1}{2} I_2$ , s).....	13.3
Silicon (metal).....	4.7	Iodine ( $\frac{1}{2} I_2$ , g).....	30.9
Phosphorus (P, g).....	35.95	Iodine (I, g).....	40.15
Sulfur (rhombic).....	7.6	Xenon.....	40.23
Sulfur (monoclinic).....	7.8	Cesium (g).....	40.28
Sulfur (S, g).....	36.04	Lanthanum.....	13.7
Chlorine ( $\frac{1}{2} Cl_2$ , g).....	26.3	Cerium.....	13.8
Chlorine (Cl, g).....	36.35	Tungsten.....	8.4
Argon.....	36.70	Osmium.....	7.8
Potassium.....	16.6	Iridium.....	8.7
Potassium (g).....	36.63	Platinum.....	10.0
Calcium.....	10.64	Gold.....	11.0
Calcium (g).....	36.71	Mercury (l).....	17.8
Titanium.....	6.6	Mercury (g).....	41.51
Chromium.....	5.8	Thallium.....	14.6
Manganese.....	7.3	Lead.....	15.53
Iron.....	6.71	Niobium.....	41.81
Cobalt.....	7.2	Thorium.....	13.6
Nickel.....	7.2	Uranium.....	11.1

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[CONTRIBUTION FROM THE LABORATORY OF ANALYTICAL CHEMISTRY, PRINCETON UNIVERSITY]

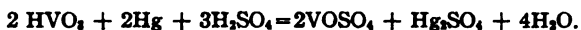
## THE REDUCTION OF VANADIC ACID SOLUTIONS WITH MERCURY

By LEROY W. MCCAY AND WILLIAM T. ANDERSON, JR.

Received February 24, 1922

### Theoretical

When a hydrochloric or sulfuric acid solution of a vanadate is shaken vigorously in the presence of mercury the solution becomes pure blue in color, the vanadium being reduced to the quadrivalent state.



If the sulfuric acid solution of the vanadate, before shaking it with mercury, be mixed with a solution of a little more sodium chloride than that equivalent to the mercurous sulfate formed, as indicated in the above equation, all the mercury oxidized during the reaction will be precipitated as mercurous chloride, which can be filtered off and a clear liquid obtained suitable for titration with potassium permanganate. The removal of the mercury present in the lower state of oxidation is necessary, for solutions of mercurous salts are oxidized by permanganate. A solution of potassium permanganate acts upon one of a vanadyl salt heated to about 80° in the following manner.



One cc. of 0.1 *N* permanganate solution is equivalent to 0.0051 g. of vanadium. The results are very accurate, for the small amount of chloride remaining in the solution has no perceptible action on the permanganate. Fifty cc. of 0.1 *N* permanganate solution shows the presence of 0.255 g. of vanadium, which is equivalent to 1.003 g. of mercury as mercurous salt, and to react with this quantity 0.2925 g. of sodium chloride is required. Assuming then that in making a determination of vanadium not more than 50 cc. of 0.1 *N* permanganate solution will be required, 0.3 g. of sodium chloride should be dissolved in the sulfuric acid solution prior to reducing it with mercury.

### Experimental

The sulfuric acid solution of vanadic acid, containing the necessary amount of sodium chloride and diluted to about 100 cc., was placed in a bottle of convenient size provided with a well fitting ground-glass stopper, 20 cc. (272 g.) of mercury was added, the bottle stoppered and the whole shaken vigorously for 5 minutes. The liquid above the slate-colored mixture of finely divided mercury and mercurous chloride was decanted into a small beaker, from which it was poured through a suction filter.

The residue in the bottle was washed four times by decantation, 20 cc. of water being used for each washing, and the washings were severally decanted into the beaker and then through the filter. The procedure here followed is identical with that described in a recent paper,<sup>1</sup> where directions for the recovery of the mercury are also given. The filtrate was then diluted to 250 cc., heated to 80–90° and titrated with permanganate to the faintest pink. Since the mixture of mercury and mercurous chloride remaining in the bottle is as active as pure mercury, the bottle after each determination was stoppered and placed aside so as to be ready at any moment for further reductions. To reduce a solution, filter it, carry out the necessary washings, heat to 90° and titrate requires about half an hour.

A solution of crystallized sodium vanadate, containing somewhat more sulfuric acid than that necessary to inhibit the separation of any metavanadates, was standardized by the sulfur dioxide<sup>2</sup> and then examined by the mercury method.

Sulfur Dioxide Method			Mercury Method		
No.	Using 0.1 N KMnO <sub>4</sub> and 25 cc. of solution	Using 0.05 N KMnO <sub>4</sub> and 10 cc. of solution	No.	Using 0.1 N KMnO <sub>4</sub> and 25 cc. of solution	Using 0.05 N KMnO <sub>4</sub> and 10 cc. of solution
	V G.	V G.		V G.	V G.
1	0.1033	0.0410	1	0.1033	0.0411
2	0.1033	0.0411	2	0.1039	0.0411
3	0.1035	0.0411	3	0.1036	0.0410
			4	0.1033	

Another solution, prepared as above outlined and standardized carefully by the sulfur dioxide method by M., was examined according to the mercury method by A. to whom the concentration of the solution was unknown. Fifty cc. of this solution was taken in each case and an approximately 0.1 N potassium permanganate solution was employed.

No.	Sulfur Dioxide Method (M)	Mercury Method (A)
	Found V G.	Found V G.
1	0.1379	0.1375
2	0.1373	0.1373
3	0.1376	0.1375
4	....	0.1373
5	....	0.1374
Av.	0.1376	0.1374

The results obtained by the two methods are practically identical.

Since hydrochloric and sulfuric acid solutions of arsenic acid are not reduced when shaken with mercury, the method may be employed for the

<sup>1</sup> THIS JOURNAL, 43, 2372 (1921).

<sup>2</sup> Treadwell-Hall, "Quantitative Analysis," John Wiley and Sons, New York, 1908, p. 501.

determination of vanadium in the presence of arsenic acid.<sup>3</sup> That the results obtained are very accurate will be evident from those given below. Sulfuric acid solutions containing the amount of sodium chloride specified were employed in all cases.

No.	Vanadium Taken* G.	$\text{KH}_2\text{AsO}_4$ G.	Vanadium Found G.
1	0.1376	0.2391	0.1375
2	0.1376	0.1564	0.1375
3	0.1376	0.3008	0.1377

\* 50 cc. of standardized sodium vanadate solution (one above employed) = 0.1376 g. of vanadium.

The presence of uranic acid or a uranyl salt does not interfere with the determination of the vanadium, for when 0.1376 g. of vanadium was taken in the presence of 0.1974 g. of monopotassium orthoarsenate and 0.2103 g. of uranyl nitrate hexahydrate, 0.1376 g. of vanadium (the amount taken) was found. Two check determinations gave 0.1374 and 0.1379 g. of vanadium. The average is 0.1376 g.

While the method has no advantages over the sulfur dioxide process so far as accuracy is concerned, it is shorter and requires less oversight than the latter. The use of sulfur dioxide and hydrogen sulfide as reducing agents is always more or less objectionable, and to expel these gases from the reduced solutions by boiling them in a current of carbon dioxide requires considerable time. It frequently happens, too, that the gases must be especially prepared when a determination of vanadium is called for, whereas the bottle containing the mercury, or mixture of mercury and mercurous chloride, is always ready, and the reduction with it complete in 5 minutes.

### Summary

1. The vanadium in a sulfuric acid solution of vanadic acid containing a relatively small amount of sodium chloride is completely reduced to the quadrivalent state when shaken in the presence of mercury for 5 minutes. Since the quantity of chloride remaining in solution after the reduction is extremely small, the method is well adapted for preparing solutions of vanadium prior to titrating them with potassium permanganate.

2. By this method vanadium can be accurately determined in the presence of arsenic and uranic acids which are not reduced by similar treatment with mercury.

<sup>3</sup> Some preliminary experiments indicate that iron also, provided the ferric sulfate solution contain the prescribed quantity of sodium chloride, may be determined rapidly and accurately in the presence of arsenates and uranyl salts. Thus, when 0.1177 g. of iron was taken in the presence of 0.2131 g. of monopotassium orthoarsenate and 0.3157 g. of uranyl nitrate hexahydrate, 0.1180 g. of iron was found. Two other determinations, made under like conditions, gave 0.1174 and 0.1186 g. of iron. The average of the three is 0.1180 g.

3. The method is shorter, more convenient, and requires less oversight than that involving the use of sulfur dioxide, and the results are fully as accurate as those obtained by the latter process.

PRINCETON, NEW JERSEY

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF PHYSICAL CHEMISTRY,  
MASSACHUSETTS INSTITUTE OF TECHNOLOGY, No. 145]

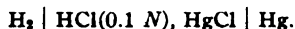
## THE EFFECT OF HYDROGEN PRESSURE ON THE ELECTRO- MOTIVE FORCE OF A HYDROGEN-CALOMEL CELL. I

By WILLIAM R. HAINSWORTH AND DUNCAN A. MACINNES

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### Introduction

This investigation is concerned with the effect of pressure of gaseous hydrogen on the potential of a cell consisting of a hydrogen electrode and a calomel electrode, both in 0.1 *N* hydrochloric acid, *i. e.*, a cell of the type



The main interest of the experiments is, of course, the effect of varying the hydrogen pressure on the potential of a reversible hydrogen electrode. In a series of investigations, the results of which have appeared in *THIS JOURNAL*, one of the authors, with his associates, has endeavored to explain the irreversible overvoltage effects occurring when hydrogen gas is formed from its ions. It became evident during these researches that equilibrium measurements, such as will be described below, are essential for a more complete knowledge of the phenomena of hydrogen overvoltage. A discussion of this relation will be reserved for another paper. The measurements are, however, of interest outside of this connection.

Lewis and Randall,<sup>1</sup> Loomis and Acree<sup>2</sup> and Ellis<sup>3</sup> have studied the effect of pressure on a reversible hydrogen electrode. They found that the usual equation

$$\Delta E = \frac{RT}{2F} \ln p \quad (1)$$

(in which  $\Delta E$  is the change of the e.m.f. of the cell produced by changing the pressure from 1 atmosphere to *p* atmospheres) is applicable within the experimental error. The range of Ellis' experiments was, however, only from 1 to 1.5 atmospheres and this was considerably greater than the ranges of pressures covered by the other investigators. In this research the pressure range was extended to 400 atmospheres.

This article will discuss the apparatus used for the measurements,

<sup>1</sup> Lewis and Randall, *THIS JOURNAL*, **36**, 1969 (1914).

<sup>2</sup> Loomis and Acree, *ibid.*, **38**, 2391 (1916).

<sup>3</sup> Ellis, *ibid.*, **38**, 737 (1916).



the experimental results, and also a more complete expression than Equation 1 for the change of e.m.f. with pressure, and one which is applicable to higher pressures.

### The Apparatus

The apparatus consisted of (a) the hydrogen-calomel cell, contained in a steel bomb, and (b) the equipment for obtaining and measuring high pressures of hydrogen, and of controlling the passage of the gas through the cell.

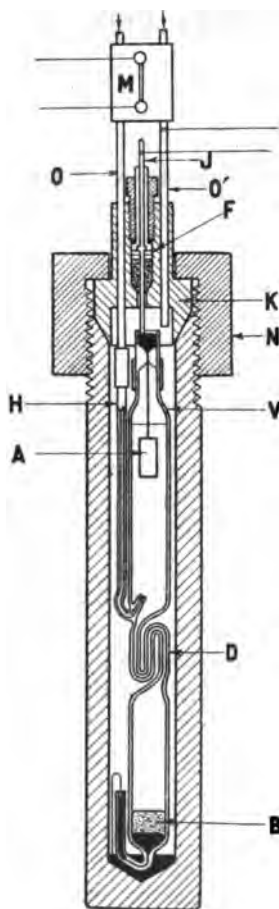


Fig. 1.

(a) **The Cell.**—The cell consisted, as is stated above, of a hydrogen electrode and a calomel electrode in 0.1 *N* hydrochloric acid. The hydrogen electrode, A in Fig. 1, was made of pure platinum gauze platinized according to the directions of Kohlrausch and Holborn.<sup>4</sup> Hydrogen passed into the cell and over the electrode through the tube H, and out through a small hole in the cell wall at V. The lower half of the cell held the calomel electrode B,<sup>5</sup> connection being made with the mercury by means of a platinum wire sealed through the glass of the cell wall. The bends in the glass tubing (at D in the figure) between the two half-cells served to prevent finely divided platinum from falling into the calomel, and to lengthen the path of diffusion for the calomel in solution, thus protecting the platinum electrode from the poisoning effect of the mercury salt. Contact was made with the calomel electrode by connecting, as shown, to mercury in the bottom of the bomb. The hydrogen electrode was connected by means of a mercury cup to a steel rod, J, passing through a specially designed insulating pressure joint, F. It was necessary to make several of these joints before one was obtained which would not give a galvanometer deflection with a potential across the insulation. Hard rubber insulators with mica washers were finally successful.

**The Bomb.**—The bomb consisted of a piece of 37 mm. hexagonal, cold-rolled steel, 25 cm. long, bored with a 19 mm. drill, and internally beveled to 60° at the top. The plug K closing the bomb and holding the insulating joint was beveled to 59.5° at the base, and was held in place with a lock nut, N, as shown. The copper tubing O and O' which was used to lead the hydrogen in and out of the cell was fastened with silver solder through holes in the plug. Connection to the potentiometer was made by wires to the insulated steel rod and to one of the copper tubes.

<sup>4</sup> Kohlrausch and Holborn, "Leitvermögen der Electrolyte," Teubner, Leipzig, 1898, p. 9.

<sup>5</sup> The mercurous chloride for the calomel electrode was precipitated from mercurous nitrate solution and was washed repeatedly with distilled water, followed by 0.1 *N* HCl solution. A saturated solution was then obtained by agitating the calomel in 0.1 *N* HCl for several days, at approximately 25°.

An annoying difficulty, during the early experiments, was that surges of gas would occur which would blow all the solution out of the upper half of the cell. These surges were largely due to the fact that the operator could not tell the rate of formation of hydrogen bubbles in the cell. Control was made possible by placing a simple microphone at the point M. This consisted of a light carbon pencil between two carbon supports, to which were connected a single dry cell and a telephone receiver. With this arrangement the breaking loose of each bubble was distinctly audible. At the higher pressures (above 100 atmospheres) this device decreased in sensitiveness for some reason that we have not been able to discover. However, regulation at these pressures was easier, as the differences were smaller between the successive pressures in the cell and those in the hydrogen reservoir.

(b) **The Apparatus for Obtaining and Measuring Hydrogen at Different Pressures.**

—The apparatus as a whole is shown diagrammatically in Fig. 2. The flow of hydrogen from the tank A (at a maximum pressure of 120 atmospheres) was controlled by the tank

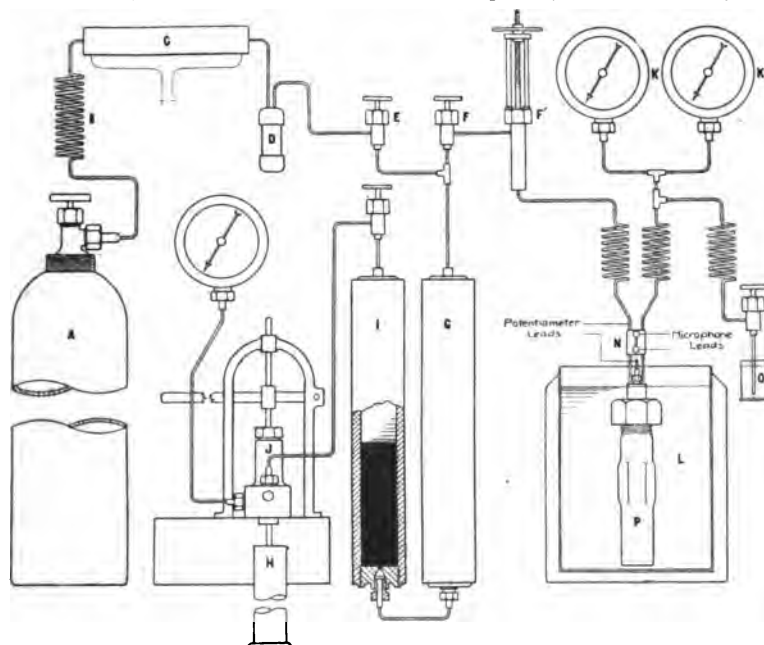


Fig. 2.

valve and the capillary copper tubing B. Traces of oxygen, in the (electrolytic) tank hydrogen, were removed by passage over platinized asbestos, maintained at  $110^{\circ}$  in the chamber C. The water formed was condensed in the drip pot D, which also served to saturate the hydrogen with water vapor at approximately  $25^{\circ}$ . The gas then passed through the needle valve E, either to the cell, through the controlling valves F and F' and the capillary tubing, or into the cylinder G, for further compression.

The higher pressures (above 120 atmospheres) were obtained by first displacing the mercury in G by hydrogen at the tank pressure, with valves F and F' closed, and then closing E and forcing oil from the graduated container H into the cylinder I, by means of the Cailletet hydraulic pump J. Care was taken to allow no oil to get into the gas chamber over the mercury, as it is probable that, if it should, frothing would result when the pressure was decreased, filling the copper tubing and other parts of the apparatus with

oil. The levels of mercury and oil were controlled by watching the amounts of oil remaining in H, and also by noting the pressures registered by the pump gage. The gas, at the higher pressure, was allowed to pass through the valves F and F', and through the cell (keeping the valve E closed) after which it escaped through the capillary tubing and the outlet valve into the atmosphere at O.

The pressures in the cell were determined by the gages K and K'. Two Crosby hydrostatic gages, and a special hydrostatic test gage, reading to 1500, 6000 and 8000 pounds per square inch, respectively, were used in various combinations, different gages, or combinations for comparison, being of service at different ranges of pressure. These gages were calibrated against a standard piston and weight apparatus such as is described by Keyes and Brownlee.<sup>6</sup> The latter gage had previously been tested against a mercury column. A slight inaccuracy in the hydrostatic gages probably developed during use, due to strain of the metal parts. It seems likely that this was the principal source of experimental errors in this work. The comparison of several series of measurements indicates that this error did not lead to uncertainties of over 0.2 mv. in the calculated potentials of the cell. However, the investigation is now being carried to higher pressures with a piston and weight apparatus (such as was used in calibrating the gages) for measuring the pressures.

The bomb P, containing the cell, was placed in a thermostat, kept at  $25^{\circ} \pm 0.1^{\circ}$ . The temperature was measured on a thermometer which had been calibrated by the Bureau of Standards. Kerosene was used in the thermostat, instead of water, to prevent rusting of the steel bomb, and to provide additional insulation.

A Leeds and Northrup potentiometer, which was carefully calibrated during the course of this work, was used to measure the e.m.f. of the cell. The standard cell used was compared, at intervals, with another standard cell which had recently been calibrated by the Bureau of Standards.

**Details of Manipulation.**—The following procedure was adopted in obtaining the experimental data. The lower half of the cell was filled (with the aid of suction) by introducing pure mercury, solid calomel and 0.1 *N* hydrochloric acid saturated with calomel. After rinsing the upper half of the cell several times with pure 0.1 *N* hydrochloric acid and nearly filling with this solution, the platinized platinum electrode, which had been washed with acid of the same concentration, was inserted. The upper half of the cell was then saturated with hydrogen at atmospheric pressure, and, if the cell potential was within 0.1 millivolt of 0.3990,<sup>7</sup> at  $25^{\circ}$ , corrected to one atmosphere of hydrogen and exactly 0.1 *N* hydrochloric acid, it was placed in the bomb, and the cone joint tightened. The hydrogen pressure was then increased. At intervals the pressure was held constant by a manipulation of the valves, which allowed a small amount

<sup>6</sup> Keyes and Brownlee, "The Thermodynamic Properties of Ammonia," Wiley and Sons, 1916, p. 10.

<sup>7</sup> Other than work on standard cells, the combination:  $H_2$  (1 atm.)  $HCl$  (0.1*N*),  $HgCl|Hg$  at  $25^{\circ}$  has received more attention than any other cell. Lewis, Brighton, and Sebastian, [THIS JOURNAL, 39, 2257 (1917)], give a summary of the values found by different investigators. Their experimental value is 0.3989. The other values are: Lewis and Randall 0.3990, Harned 0.3991, Loomis and Meacham 0.3988, Ellis 0.3989. All these values have been corrected for the vapor pressure of water. This correction, however, soon becomes negligible when the pressure is raised above 1 atmosphere.

of hydrogen to pass through the cell until a constant e.m.f. was obtained. Half an hour after reaching a constant pressure a constant potential (within 0.02 mv.) was observed, and this did not change further as long as the pressure was held at that point. After reaching the maximum pressure for a series, potential measurements were made while lowering the pressure, which was reduced so slowly that substantial equilibrium was maintained throughout.

### Experimental Data

Four successful "runs," or series of measurements, were made. These will be called Expts. 1, 2, 3, and 4, respectively. In Expt. 1 the maximum pressure obtainable was that of the tank of hydrogen A (Fig. 2) since the mercury pump I, G, had not yet been installed. Expt. 2 was a repetition of Expt. 1, except that measurements were made only at 1 atmosphere and at the maximum tank pressure.

For Expt. 3, the mercury pump was added to the apparatus and readings at higher pressures than the tank pressure were obtained. The range, however, did not extend as high as was anticipated due to a leak which developed in one of the gages.

In Expt. 4 a maximum of 406 atmospheres was reached. After obtaining this maximum the pressure was very slowly reduced to that of the atmosphere, substantial equilibrium being attained at all points down to about 2 atmospheres.

It was found in every case except Expt. 2 that on reducing the pressure to about 3 atmospheres, bubbles formed in the bent tube connecting the two halves of the cell. This broke the electrical circuit. The effect was undoubtedly due to the diffusion of dissolved hydrogen into the tubes and its appearance as the gas phase at low pressures. In Expt. 2, however, the time elapsing between the initial and final reading was made a minimum, thus reducing this diffusion, and no bubbles formed. In this experiment, the "return" value of the e.m.f. agrees within 0.1 mv. with the initial value. An examination of the agreement of the values obtained while increasing and decreasing the pressure shows, with certainty, that equally good agreement in the other three experiments would have been found if the return measurements below 3 atmospheres could have been made.

The results of the four experiments are summarized in Table I. In the first column is given the number of the experiment. The letter *I* indicates that increases of pressure were made before and after the measurements recorded, *D* represents measurements with corresponding decreases of pressure, and *M* the maximum pressure of the particular experiment. The "return" value obtained in Expt. 2 is represented by  $2R$  in the table.

Expts. 2, 3 and 4 were made with 0.0993 *N* acid in the cell. A cor-

rection of  $-0.0004$  v. was necessary for these experiments to bring all the measurements to a basis of exactly  $0.1 N$ . This small correction can be obtained, without any error, from a consideration of the activities of hydrochloric acid at the concentrations involved. The measurements for Expt. 1 were made with exactly  $0.1 N$  acid. The values for the e.m.f. as given in Table I include this correction and, for the initial determination of each series, the usual corrections for the difference between one atmosphere and the barometer reading, and also for the vapor pressure of the solution.

TABLE I  
MEASUREMENTS OF THE CELL  $H_2 | HCl (0.1 N), HgCl | Hg$  AT  $25^\circ$  AND AT DIFFERENT PRESSURES

Expt.	<i>P</i> Atm.	E.m.f.	Expt.	<i>P</i> Atm.	E.m.f.	Expt.	<i>P</i> Atm.	E.m.f.
1	1	0.3990	4 <i>D</i>	23.1	0.4392	4 <i>D</i>	122.2	0.4611
2	1	0.3990	4 <i>D</i>	24.0	0.4396	3 <i>D</i>	169.8	0.4654
3	1	0.3990	1 <i>I</i>	43.2	0.4472	3 <i>M</i>	199.6	0.4677
4	1	0.3990	1 <i>I</i>	76.5	0.4547	4 <i>I</i>	209.6	0.4683
2 <i>R</i>	1	0.3991	3 <i>I</i>	85.4	0.4563	4 <i>D</i>	216.8	0.4690
4 <i>D</i>	2.2	0.4091	4 <i>D</i>	89.6	0.4568	4 <i>D</i>	268.5	0.4720
4 <i>D</i>	2.9	0.4127	1 <i>I</i>	95.8	0.4577	4 <i>I</i>	281.1	0.4725
4 <i>D</i>	7.6	0.4251	2 <i>M</i>	106.7	0.4594	4 <i>I</i>	337.2	0.4751
1 <i>I</i>	16.3	0.4348	1 <i>M</i>	112.0	0.4604	4 <i>M</i>	406.2	0.4779

### Theoretical Discussion

If we apply the first law of thermodynamics to a reversible process which includes an electrical work term,  $EdC$ , in which  $E$  is the electromotive force, and  $C$  the current (coulombs) and substitute the relation,  $dQ = TdS$  between the heat absorbed,  $Q$ , the entropy  $S$  and the absolute temperature  $T$ , we obtain,

$$dU = TdS - pdV - EdC \quad (2)$$

in which  $U$ ,  $p$  and  $V$  are the total energy, the pressure and the volume, respectively.

The thermodynamic potential  $F_p$ ,<sup>8</sup> for which  $p$  and  $T$  are the independent variables, is defined by the relation,

$$F_p = U - TS + pV \quad (3)$$

Differentiating and substituting in (2) we have

$$dF_p = Vdp - SdT - EdC \quad (4)$$

At a constant temperature, the following reciprocal relation between the differential quantities holds, if  $dF_p$  is a total differential

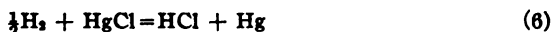
$$\left(\frac{\partial E}{\partial p}\right)_{C,T} = -\left(\frac{\partial V}{\partial C}\right)_{p,T} \quad (5)$$

<sup>8</sup> This is the free energy as used by G. N. Lewis [THIS JOURNAL, 35, 1 (1913)] but not as defined by Helmholtz. In the process of the cell we are considering, it is the electrical work,  $nEC$ , when the cell operates at constant pressure.

In a cell operating at constant pressure and temperature the change of volume is determined by the chemical reaction occurring, and is dependent only on the amount of current passing through the cell. For that reason  $\left(\frac{\partial V}{\partial C}\right)_{P,T} = \frac{\Delta V}{F}$  in which  $\Delta V$  is the change of volume during the passage of  $F$  faradays. Equation 5, therefore, becomes

$$\left(\frac{\partial E}{\partial p}\right)_{C,T} = -\frac{\Delta V}{F} \quad (5a)$$

When the cell,  $\text{H}_2|\text{HCl} (0.1 N), \text{HgCl}|\text{Hg}$ , operates, the reaction



takes place. Equation 5a shows that the e.m.f. of the cell increases with increasing pressure on the system if the volume decreases when the above reaction proceeds, and *vice versa*.

If we allow the cell to operate reversibly at constant pressure and temperature until one faraday of electricity passes, the following total volume change,  $\Delta V$ , occurs,

$$\Delta V = (\bar{V}_{\text{HCl}} + V_{\text{Hg}}) - (\frac{1}{2}V_{\text{H}_2} + V_{\text{HgCl}}), \quad (7)$$

in which  $\bar{V}_{\text{HCl}}$  represents the partial molal volume of hydrochloric acid in a 0.1  $N$  hydrochloric acid solution, and the remaining terms are the molal volumes of the substances indicated by the corresponding subscripts. In order to integrate Equation 5a it is necessary to express the separate terms in Equation 7 as functions of the pressure. These terms will be considered separately in the following paragraphs.

**The Molal Volume of Hydrogen,  $V_{\text{H}_2}$ , as a Function of the Pressure.**—The most important term in Equation 7 is, of course, the volume of gaseous hydrogen. Several equations of state were investigated with regard to their agreement with the existing data on the pressure-volume relations for this gas. The Keyes<sup>9</sup> equation of state was found to be nearest in agreement with the existing experimental data under the conditions of our experiments. The Keyes equation is generally given in the form

$$P = \frac{RT}{v-\delta} - \frac{A}{(V-l)^2} \quad (8)$$

in which  $\delta = \beta e^{-\alpha/v}$  and  $\alpha, \beta, A$  and  $l$ , are characteristic constants. For hydrogen, when  $V = \text{cc. per g.}$ ;  $\alpha = 2.898$ ,  $\beta = 9.619$ ,  $A = 3.91 \times 10^4$ ,  $l = 1.18$  and  $R = 40.72$ . Using the above data, the  $pV$  product, obtained by assuming values of  $V$  and solving for  $p$ , was plotted against  $p$ , and the following equation obtained for hydrogen at 25°,

$$pV = 298.1 R (1 + 0.00057p - 1 \times 10^{-8} p^2). \quad (9)$$

Equation 9 is in satisfactory agreement with the interpolated values

<sup>9</sup> Keyes, *Proc. Nat. Acad. Sci.*, **3**, 323 (1917); *THIS JOURNAL*, **46**, 589 (1919).

obtained from the experimentally determined  $pV$  products at  $0^\circ$  and  $100^\circ$ . Although the values obtained by Amagat<sup>10</sup> and Holborn<sup>11</sup> are slightly higher, for pressures over 200 atmospheres, than those given by Equation 9, the Keyes equation is in good agreement, over a large pressure and temperature range, with the data obtained by Witkowski,<sup>12</sup> and by Onnes and Braek.<sup>13</sup> For this reason Equation 9 was chosen in preference to an empirical equation based on experimental determinations of the  $pV$  product, interpolated between  $0^\circ$  and  $100^\circ$  approximately. There are no data recorded for  $25^\circ$ .

**The Partial Molal Volume,  $V_{\text{HCl}}$  of Hydrochloric Acid.**—To evaluate  $\bar{V}_{\text{HCl}}$ , the partial molal volume<sup>14</sup> of hydrochloric acid, the following expression for the volume of the solution at any concentration and pressure can be used,

$$V = \frac{1000 + CM}{D_0} (1 - \alpha p) \quad (10)$$

in which  $C$  is the weight concentration, (moles per 1000 g. of water),  $M$  the equivalent weight of hydrochloric acid,  $D_0$  the density of the solution at atmospheric pressure, and  $\alpha$  is the compressibility of the solution.

Then,

$$\left(\frac{\partial V}{\partial C}\right)_p = \bar{V}_{\text{HCl}} = \frac{D_0 M - (1000 + CM) \frac{dD_0}{dC}}{D_0^2} (1 - \alpha p). \quad (11)$$

In order to evaluate  $dD_0/dC$  it is necessary to make use of density determinations of hydrochloric acid solutions, a series of which are given (for  $25^\circ$ ) in Table II.

TABLE II

HCl Conc.	$d_4^{25}$	Observer Ref.	HCl Conc.	$d_4^{25}$	Observer Ref.
		Landolt-Börnstein			
0.0000	0.997071	"Tabellen"	0.1000	0.99886	16
0.0050	0.997140	15	0.1004	0.9989	17
0.0100	0.997224	15	0.3376	1.0031	17
0.0200	0.997405	15	0.5000	1.00591	16
0.0400	0.997779	15	0.5095	1.0059	17
0.1000	0.998868	15			

A plot of these data is almost exactly a straight line and gives for the

<sup>10</sup> Amagat, *Ann. chim. phys.*, [6] 29, 68 and 505 (1893).

<sup>11</sup> Holborn, *Ann. Physik.*, 63, 674 (1920).

<sup>12</sup> Witkowski, (1905), from Landolt and Börnstein, "Tabellen."

<sup>13</sup> Onnes and Braek, *Versl. Amsterdam*, 30, 411 (1907).

<sup>14</sup> This is the change of volume which would occur if one mol of HCl gas were added to an infinite volume of a solution of the substance at the given concentration.

<sup>15</sup> Ansdell, *Chem. News*, 41, 75 (1880).

<sup>16</sup> C. E. Ruby, private communication.

<sup>17</sup> Ellis, *THIS JOURNAL*, 38, 737 (1916).

slope,  $\frac{\Delta D_0}{\Delta C}$ , the value 0.0175 which may, in this case, be set equal to  $\frac{dD_0}{dC}$ . If we make the assumption that  $\alpha$  is equal to the compressibility of water, which has a mean value of  $44 \times 10^{-6}$  between 1. and 400 atmospheres, then Equation 11 reduces to

$$\bar{V}_{\text{HCl}} = 18.89 - 8.3 \times 10^{-4} p \quad (12)$$

for a 0.1 *N* hydrochloric acid solution. This ignores a possible change of the partial molar volume due to solubility of the hydrogen gas by which the pressure is applied. This point will be referred to later.

**The Molal Volumes of Mercury and Calomel.**—From the density data of Thiesen, Scheel and Sell<sup>18</sup> the molar volume of mercury was found to be 14.82 at 25°. A simple computation shows that the compressibility of mercury, in the pressure range of our experiments, can be neglected, the effect of a pressure of 400 atmospheres leading to a correction of only 0.005 mv. on the computed potential of the cell.

The density of solid calomel was redetermined for this investigation. Three determinations gave, respectively, 7.155, 7.153 and 7.152, having an average value of 7.153 at 25° referred to water at 4°. This is concordant with the value, 7.151, given by Timofejew.<sup>19</sup> Using the mean value of the density we obtain 33.00 cc. for the molal volume of calomel. The compressibility of calomel has apparently not been determined, but it must be of the same order of magnitude as that of mercury or smaller. Further, since mercury and calomel are on opposite sides of the equation for the reaction occurring in the cell, the resultant effect of the compressibilities of these substances must be smaller than the effect of either one.

**The Equation for the Change of Potential with Pressure.**—When we substitute the values of the specific volumes obtained in the foregoing paragraphs into Equation 7 we obtain for the change of volume when one equivalent of current passes through the cell, at the pressure  $p$ , the following expression.

$$\begin{aligned} \Delta V &= (18.89 - 8.3 \times 10^{-4} p + 14.82) - \\ &\quad \left[ 33.00 + 12230 \left( \frac{1}{p} + 0.00057 - 1 \times 10^{-4} p \right) \right] \\ &= - \frac{12230}{p} - 6.26 - 7.1 \times 10^{-4} p \end{aligned}$$

This gives, on substituting in Equation 5a,

$$\Delta E = \frac{0.1013}{F} \int_1^p \left( \frac{12230}{p} + 6.26 + 7.1 \times 10^{-4} p \right) dp$$

<sup>18</sup> Thiesen, Scheel and Sell, *Wiss. Abh. P.T.R.*, 2, 184 (1895).

<sup>19</sup> Timofejew, *Z. physik. Chem.*, 78, 299 (1911).



and integrating between the limits  $p$  and 1 we obtain

$$\Delta E = 0.02958 \log p + 6.56 \times 10^{-4} (p-1) + 3.7 \times 10^{-10} (p^2 - 1) \quad (13)$$

This appears to be the most complete thermodynamic treatment that can be obtained using the available experimental data. As stated above, it does not include effects due to the change of volume of the acid solution due to the solubility of the hydrogen. It will be noted that the first term of this equation follows directly from the expression  $RT/2F \ln p$  of Equation 1, and that the other terms are of appreciable magnitude only at comparatively high pressures.

The data of Table I are represented graphically in Fig. 3. Curve 1 of that figure is the result of plotting the observed voltages against the logarithm of the pressure in atmospheres. Up to 100 atmospheres

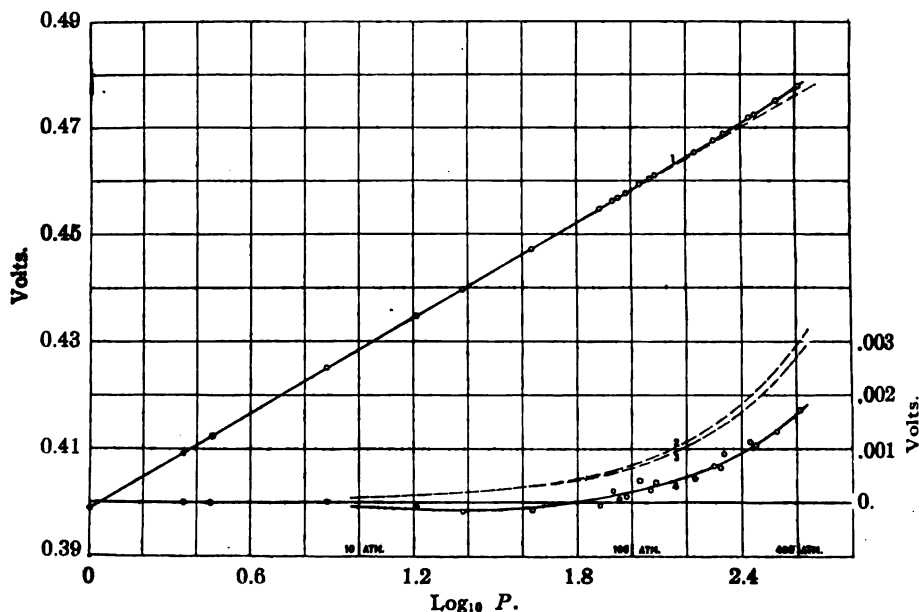


Fig. 3.

this is a straight line, within the experimental error, the slope of which is exactly, 0.02958 ( $= 2.303RT/2F$ ) required by Equation 1. However, above 100 atmospheres there is a slight but definite divergence from this linear relation. The dotted line is a prolongation of the straight line below 100 atmospheres. A straight line throughout the range of the measurements would result, of course, if the hydrogen were a perfect gas and if the compressibilities of the other substances entering into the reaction of the cell were negligible or compensating.

In Curve 4 the divergences, from the simple logarithmic relation, are plotted on a much larger scale. The base line corresponds to no divergence

1. The first of these is the  
 2. second of these is the  
 3. third of these is the  
 4. fourth of these is the  
 5. fifth of these is the  
 6. sixth of these is the  
 7. seventh of these is the  
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 9. ninth of these is the  
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of hydrogen, is necessary. This correction is at present under investigation.

The study of the variation of the potential of the cell with pressure is being extended to higher pressures.

CAMBRIDGE 39, MASSACHUSETTS

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF Breslau]

## NITROSYL SELENIC ACID

By JULIUS MEYER AND WALTER WAGNER

Received February 27, 1922

Since selenic acid, in many respects, is similar to sulfuric acid, it is to be expected that it would give with nitrous acid an anhydrous compound corresponding to nitrosyl sulfuric acid,  $\text{SO}_2(\text{OH})(\text{ONO})$ . Victor Lenher and J. H. Mathews,<sup>1</sup> by treating selenic acid of the strength of about 83% with liquid nitrogen tetroxide ( $\text{N}_2\text{O}_4$ ) at a temperature obtained by the use of solid carbon dioxide, have prepared dinitrosyl selenic acid  $\text{SeO}_2(\text{ONO})_2$  which is stable below  $-13^\circ$  and which is described as an easily decomposable compound of blue color. Previous to our experiments, the mononitrosyl compound had not been described.

The existence of a new compound between selenic and nitrous acid can be shown by dissolving solid sodium nitrite in ice-cold selenic acid of about 95% strength. The salt dissolves without evolution of gas and without change in color of the liquid. On diluting the solution with water, red oxides of nitrogen are evolved in large amounts, a behavior resembling the decomposition of "lead chamber crystals" by water.

In order to prepare nitrosyl selenic acid we brought together, in absence of water, liquid nitrogen trioxide ( $\text{N}_2\text{O}_3$ ) and selenic acid prepared by the method of Meyer and Moldenhauer.<sup>2</sup> While sulfur dioxide reacts readily with nitric acid to form nitrosyl sulfuric acid, selenium dioxide in our experience does not react similarly.

In order to prepare nitrosyl selenic acid, liquid nitrogen trioxide is poured into 100% selenic acid, the former being in great excess. The greater part of the excess of the nitrogen trioxide is evaporated from the white crystalline mass by vigorous stirring, after which the last trace of excess of the oxides of nitrogen is removed by spreading the crystals on a porous plate and evaporating, at as low a temperature as possible, in a vacuum desiccator. The white crystals can be preserved in dry, sealed tubes, but decompose when warmed, with an evolution of the red oxides of nitrogen. Moisture decomposes the crystals with a similar evolution and the solution when treated with barium chloride yields barium selenate. The crystals irritate the skin.

<sup>1</sup> Lenher and Mathews, *THIS JOURNAL*, 28, 516 (1906).

<sup>2</sup> Meyer and Moldenhauer, *Z. anorg. Chem.*, 116, 193 (1921).

**Analysis.**—Weighed quantities of the crystals were decomposed with water in a Meyer-Jannek apparatus.<sup>1</sup> The free selenic acid was reduced to selenious acid by heating with conc. hydrochloric acid, after which it was reduced to elementary selenium by hydrazine. Two analyses yielded 45.0 and 44.5% of selenium, while  $\text{SeO}_2(\text{OH})(\text{ONO})$  requires 45.3% of selenium.

For the determination of nitrogen, weighed quantities of the crystals were shaken in a closed bottle with a solution of sodium hydroxide until the nitrogen oxide fumes which were evolved had again been absorbed. The resulting solution was treated with a measured excess of potassium permanganate solution, and after oxidation of the nitrous to the nitric acid, the excess of permanganate was titrated back by means of oxalic acid. In two samples, 7.3 and 7.4% of nitrogen were found. Nitrosyl selenic acid requires 8% of nitrogen. Considering the methods of analysis used, the results are sufficiently accurate.

Nitrosyl selenic acid,  $\text{SeO}_2(\text{OH})(\text{ONO})$ , is decomposed by water. It is readily soluble in conc. selenic and conc. sulfuric acids. Nitrosyl sulfuric acid is also soluble in these acids, and both compounds are soluble in absolute alcohol but not in ether. At  $80^\circ$ , nitrosyl selenic acid melts with decomposition. This is also the melting point of nitrosyl sulfuric acid and is considerably higher than that of pure selenic acid, which is  $58^\circ$ .

Nitrosyl selenic acid is very reactive and with certain of the organic amines readily forms compounds, which we are studying.

BRESLAU, GERMANY

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[CONTRIBUTION FROM THE KENT CHEMICAL LABORATORY OF THE UNIVERSITY OF CHICAGO]

## THE SEPARATION OF ISOTOPES BY THERMAL AND PRESSURE DIFFUSION

BY ROBERT S. MULLIKEN<sup>1</sup>

Received March 1, 1922

### Introduction

With the ultimate aim of obtaining extensive separations of isotopes, a careful preliminary study, both theoretical and experimental, is being made, in order to find the best practical method or methods. In a previous paper by Mulliken and Harkins<sup>2</sup> the theory was developed and equations obtained for the change of composition and atomic weight for the fractions obtained when a mixture of isotopes is subjected to a process of irreversible evaporation, molecular effusion, molecular diffusion, or gaseous diffusion. A rather complete summary of the possible methods for separating isotopes was also given (p. 62). In the present paper, the theory of the method of thermal diffusion and that of the centrifugal

<sup>1</sup> Meyer and Jannek, *ibid.*, **83**, 51 (1913).

<sup>2</sup> National Research Fellow in Physical Chemistry.

<sup>3</sup> Mulliken and Harkins, *THIS JOURNAL*, **44**, 37 (1922).

method, as applied to the separation of isotopes, are rather fully discussed. Equations analogous to those for the other methods of separation are obtained, and used in a study of the applicability of the methods to various isotopic elements. Conclusions are reached as to the practical value of the two methods.

### Equations for Diffusion and Evaporation Processes

The most important equations obtained in the previous paper will here be reviewed briefly, using the same equation numbers as there given.

For a mixture of *two* isotopes, the equations for the residue in an evaporation or diffusion process are, 
$$\Delta x_2 = \frac{(1-k) x_1 x_2}{2(x_1 + k x_2)} \cdot \ln C = A \ln C \quad (6)$$

or approximately, 
$$\Delta x_2 = \frac{(M_2 - M_1) x_1 x_2}{2M} \cdot \ln C \quad (6a)$$

and 
$$\Delta M = A(M_2 - M_1) \ln C = B \ln C \quad (7)$$

or approximately, 
$$\Delta M = \frac{(M_2 - M_1)^2 x_1 x_2}{2M} \cdot \ln C \quad (7a)$$

Similar relations hold for a mixture of any number of isotopes. The  $x$ 's denote mol-fractions, the  $M$ 's atomic or molecular weights;  $k = \sqrt{M_1/M_2}$ ; and  $C$ , the "cut," is the ratio of the initial to the final number of mols present in the residue.<sup>1</sup> The subscript 1 refers to the lighter, 2, to the heavier isotope.  $M$  without subscript stands for the ordinary, average, atomic or molecular weight.  $B$  is called the separation coefficient.

For the diffused or evaporated material, the equations are,

$$-\Delta x_2 = A \ln C / (C-1) \quad (15)$$

$$\text{and } -\Delta M = B \ln C / (C-1) \quad (16)$$

The *total difference* in atomic weight<sup>4</sup> between the two fractions is then

$$\Delta \Delta M = \Delta M - (-\Delta M) = [B + B/(C-1)] \cdot \ln C = B \cdot C \ln C / (C-1) \quad (19)$$

$$= \frac{(M_2 - M_1)^2 x_1 x_2}{2M} \cdot \frac{C}{C-1} \ln C, \text{ nearly} \quad (19a)$$

For  $C=1$ ,  $\Delta \Delta M=B$ ; for  $C=2$ ,  $\Delta \Delta M=2B \ln 2=1.386 B$ ; for  $C=4$ ,  $\Delta \Delta M=(8/3) B \ln 2=1.848B$ ; etc. The value for  $C=2$  is of the most interest, since it corresponds to a division of the material into two equal fractions. All the above equations hold for a mixture of more than two isotopes, except that the expressions for  $A$  and  $B$  are more complex (see previous paper).

### Thermal Diffusion

It has been shown theoretically<sup>5</sup> and experimentally<sup>6,7</sup> that if a gaseous

<sup>1</sup> In the case of gaseous diffusion, the numerical factor in the denominator is probably always greater than 2. This factor is equal to the exponent  $c$  in the value of  $k$ : in general,  $k = \sqrt[c]{M_1/M_2}$ .

<sup>4</sup> This equation was not given in the previous paper.

<sup>5</sup> Enskog, *Physik. Z.*, 12, 538 (1911); *Ann. Physik*, 38, 750 (1912); and Chapman, *Phil. Trans.*, 217A, 115 (1916); *Phil. Mag.*, [6] 34, 146 (1917).

<sup>6</sup> Chapman and Dootson, *Phil. Mag.*, [6] 33, 248 (1917).

<sup>7</sup> Ibbs, *Proc. Roy. Soc.*, 99, 385 (1921).

mixture is present in a container, one portion of which is kept hot, and another cold, an equilibrium state is attained in which there is an increased concentration of the *larger* or *heavier* molecules at the cold end, and *vice versa*. For a mixture of two isotopes, Chapman deduces<sup>8</sup> the relation (here altered to conform to the present notation),

$$\Delta x_2 = k_1 \ln T'/T = (17/3) \cdot \frac{M_2 - M_1}{M_2 + M_1} \cdot \frac{x_1 x_2}{9.15 - 8.25 x_1 x_2} \cdot \ln T'/T, \quad (20)$$

for molecules which behave like elastic spheres,  $\Delta x_2$  standing for the difference between the values of  $x_2$  in the regions at the two temperatures. Actually, in the case of a mixture of hydrogen and carbon dioxide,  $k_1$  proves to be only about  $1/2$  or  $1/3$  as large because the molecules do not behave as assumed. Approximately, since

$$\Delta M = (M_2 - M_1) \Delta x_2, \quad \Delta_t M = K \cdot \frac{(M_2 - M_1)^2 x_1 x_2}{2 M_1} \cdot \ln T'/T = K B \ln T'/T \quad (21)$$

The analogy to Equations 7A and 19 is obvious. Except for some variability in  $K$  for different types of molecules, the separation coefficient  $KB$  for thermal diffusion depends in nearly the same way on the mol-fractions and molecular weights of the isotopes as does the coefficient  $B$  for ordinary diffusion. Thermal diffusion is apparently however a much weaker agent than ordinary diffusion, under any practicable conditions, for if  $K = 1/4$ , a reasonable estimate, then a temperature ratio of 15.5 (e. g.,  $80^\circ$  absolute against  $1240^\circ$  absolute) will give  $\Delta_t M = (1/4)B \ln 15.5 = 0.693 B = B \ln 2$ . Even if the mixture is divided almost wholly into two equal fractions at the two extreme temperatures, the value of  $\Delta_t M$  is only *half* as great as the corresponding value ( $2B \ln 2$ ) of  $\Delta M$  for a cut of 2 by one of the diffusion methods previously considered. This is in spite of the very large temperature ratio, corresponding to a range from liquid air temperature to  $1000^\circ$ . Evidently the method of thermal diffusion cannot compete<sup>9</sup> with the other diffusion methods as a means of separating isotopes.

**Evaporative Thermal Diffusion.**—Probably the most favorable way to apply thermal diffusion would be to use a method of procedure similar to that proposed in the case of centrifugal separation, *viz.*, to have a supply of the liquid mixture in the cold bulb, and to draw off gas very slowly from the hot bulb. The rate of separation<sup>10</sup> would be the same as for an ordinary diffusion or an irreversible evaporation having a separation coefficient equal to  $\Delta_t M$ . As a matter of theoretical interest it is intended to test this method of "evaporative thermal diffusion" experimentally with mercury. If the process of drawing off the gas took place through a

<sup>8</sup> Chapman, *Phil. Mag.*, [6] 38, 182 (1919).

<sup>9</sup> The method of thermal diffusion can, it is true, be adapted to rapid continuous operation, but probably only at a large sacrifice of efficiency (cf. Ibbs, Ref. 7).

<sup>10</sup> Compare discussion under centrifugal separation.

porous wall, the effect of ordinary diffusion would be added to that of thermal diffusion, and the result would be the same as for an ordinary diffusion with a separation coefficient  $(B + \Delta_p M)$ , instead of  $B$ . This increase would, however, hardly be worth the added difficulties.

### Pressure Diffusion

**Development of Equations.**—The problem of the separation of isotopes by "pressure diffusion," that is, by virtue of variation of composition along a pressure gradient, due either to a gravitational field or to centrifugal force, has been discussed by Lindemann and Aston,<sup>11</sup> and by Chapman,<sup>8</sup> who compares the method with that of thermal diffusion. Lindemann and Aston derive equations applicable to a *gaseous* mixture of *two* isotopes. These, slightly modified, and transcribed, are as follows.

For gravitational separation,  $r = e^{\frac{g \Delta_p (M_2 - M_1)}{RT}}$ , (22) and for centrifugal separation  $r = e^{\frac{v^2 (M_2 - M_1)}{2RT}}$  (23). Here  $r$  stands<sup>12</sup> for  $\frac{x_2/x_1}{(x_2)_0/(x_1)_0}$ , the sub-

script  $o$  referring to the point of reference, for example, the center of the centrifuge, or the level of the earth;  $v$  is the peripheral velocity. Chapman gives the equation (here transcribed), applicable to any type of pressure diffusion,

$$\Delta_p x_2 = k_p \ln p/p_0 = \frac{(M_2 - M_1)x_1 x_2}{M_1 x_1 + M_2 x_2} \cdot \ln p/p_0, \quad (24)$$

analogous to his equation for thermal diffusion.

Equations can be derived for the case of pressure diffusion, analogous to those for other types of diffusion, which show clearly the factors on which the change of atomic weight depends. It will be best to go through with the derivation from the beginning, since the methods and notation are different from those of Lindemann and Aston, and of Chapman. For a gaseous mixture of *two* isotopes at total pressure  $p$  and density  $\rho$ ,

subjected to centrifugal action,  $dp_1 = \frac{v^2 \rho_1 dr}{r} = \rho_1 \omega^2 r dr = \frac{M_1 \rho_1 \omega^2 r dr}{RT}$ .

Here  $p_1$  and  $\rho_1$  refer to the partial pressure and density of the lighter isotope, and  $v$ ,  $\omega$ , and  $r$ , denote respectively linear velocity, angular velocity, and radial distance. An analogous equation holds for the heavier

isotope. The above equation gives  $\frac{dp_1}{p_1} = d \ln p_1 = \frac{M_1 \omega^2}{RT} r dr$ . Then

$$\frac{\ln p_1}{(p_1)_0} = \frac{M_1 \omega^2 (r^2 - r_0^2)}{2RT} = \frac{M_1 (v^2 - v_0^2)}{2RT}. \quad (25)$$

<sup>11</sup> Lindemann and Aston, *Phil. Mag.*, [6] 37, 523 (1919).

<sup>12</sup> The quantity  $r$  is analogous to the "enrichment ratio" of Rayleigh (see Mulliken and Harkins, Ref. 2), but differs in that it corresponds to  $\Delta_p M$  instead of to  $\Delta M$ .

If  $r_0 = 0$ ,  $v_0 = 0$ . By combining Equation 25 with the corresponding expression in terms of  $p_2$ , and putting  $v_0 = 0$ , Lindemann and Aston's relation (23) can be obtained. The following relation, which will be useful in another connection, can also be seen to hold approximately,

$$\ln \frac{p}{p_0} = \frac{M(v^2 - v_0^2)}{2RT}. \quad (26)$$

Chapman's relation (24) for  $\Delta_p x_2$  can be obtained by a derivation analogous to that used in the paper of Mulliken and Harkins in arriving at Equations 2, 5, and 6. Thus from the equations above given for  $dp_1/p_1$  and  $dp_2/p_2$ ,  $dp_2/p_2 = (M_2/M_1) \cdot dp_1/p_1$ . Then since  $p_1 = px_1$  and  $p_2 = px_2$ , we have  $\frac{pdx_2 + x_2dp}{px_2} = \frac{M_2}{M_1} \cdot \frac{pdx_1 + x_1dp}{px_1}$ . From this point the derivation is precisely analogous to that used in obtaining Equation 6 of the previous paper, everything being unchanged except that  $p$  everywhere replaces  $N$  ( $p_0/p$  replaces  $N_0/N = C$ ), and  $M_2/M_1$  replaces  $\sqrt{M_1/M_2} = k$ . Thus we obtain the relation, formally analogous<sup>13</sup> to Equation 6,

$$\Delta_p x_2 = \frac{(1 - M_2/M_1)x_1x_2}{x_1 + (M_2/M_1)x_2} \cdot \ln \frac{p}{p_0}.$$

Then

$$\Delta_p M = (M_2 - M_1) \Delta_p x_2 = \frac{(M_2 - M_1)^2 x_1 x_2}{M} \cdot \ln \frac{p}{p_0} \quad (27)$$

which is formally analogous<sup>13</sup> to Equations 7 and 7A. Combining (26) and (27), there results the approximate relation<sup>14</sup> for the difference in atomic weight at points  $r$  and  $r_0$

$$\Delta_p M = \frac{(M_2 - M_1)^2 x_1 x_2 (v^2 - v_0^2)}{2RT} = P(v^2 - v_0^2) = P\omega^2 (r^2 - r_0^2). \quad (28)$$

For the general case of a mixture of several (atomic, or molecular) isotopes, the corresponding relation<sup>15</sup> is  $\Delta_p M = \frac{\Sigma(M_a^2 x_a) - [\Sigma(M_a x_a)]^2}{2RT}$ .

<sup>13</sup>  $\Delta_p x_2$  and  $\Delta_p M$  are really more nearly analogous to  $\Delta x_2$  and  $\Delta M$  (compare Equation 19), in *physical meaning*, than to  $\Delta x_2$  and  $\Delta M$ .

<sup>14</sup> Similarly, for *gravitational* separation, which is of course not a *practical* method,  $\Delta_p M = (M_2 - M_1)^2 x_1 x_2 g(h - h_0)/RT = 2P g \Delta h$  (29).

<sup>15</sup> This is obtained as follows. Analogous to Equation 6' of the previous paper, we have here  $\Delta_p x_a = \frac{x_a(S - k'_a)}{S} \cdot \ln p_0/p$ . Here  $k'_a = M_a/M_1$ , and  $S = \Sigma x_a k'_a =$

$\frac{\Sigma x_a M_a}{M_1} = \frac{M}{M_1}$  and  $S - k'_a = (M - M_a)/M_1$ . So  $\Delta_p x_a = \frac{x_a(M_a - M)}{M} \cdot \ln \frac{p}{p_0} = \frac{x_a(M_a - M)(v^2 - v_0^2)}{2RT}$ . Now  $\Delta_p M = \Sigma(M_a - M_1) \Delta x_a = \frac{v^2 - v_0^2}{2RT} \cdot \Sigma[x_a(M_a - M)(M_a - M_1)]$ .

The summation can be expanded to  $\Sigma x_a M_a^2 - M \Sigma x_a M_a - M_1 \Sigma x_a M_a + M M_1 \Sigma x_a =$



$$(v^2 - v_0^2) = \frac{\Sigma(M_a^2 x_a) - M^2}{2RT} \cdot (v^2 - v_0^2) = \frac{\overline{M^2} - (\overline{M})^2}{2RT} (v^2 - v_0^2) = \frac{\Sigma_a \Sigma_b x_a x_b (M_a - M_b)^2}{2RT} \\ (v^2 - v_0^2) = P'(v^2 - v_0^2). \quad (28')$$

The subscripts *a* and *b* here refer independently to each isotope in turn.<sup>16</sup> In the last expression, each like term of the summation is to be taken *only once* (in the complete summation each appears twice). The expression for *P*, although different in form from that for *P'*, is obtainable from the latter as a special case.<sup>17</sup> The only approximations in deriving the expressions for *P* and *P'* are those involved in the use of Equation 26, and that of using a differential quantity  $dx_a$  as a finite increment  $\Delta_p x_a$ . The error involved is only a few per cent. unless  $\Delta_p M$  is large, in which case the change of *P* and *P'* with *M* can be allowed for by inserting a term obtained by taking the second derivative. (Compare discussion and Equations 9 and 10 of the previous paper.)

**Comparison of Centrifugal and Ordinary Separation Methods and Coefficients.**—The following values of the "centrifugal separation coefficients" (*P* or *P'*) have been calculated for several elements at 20°: Li,  $1.16 \times 10^{-12}$ ; B,  $1.85 \times 10^{-12}$ ; Ne,  $7.38 \times 10^{-12}$ ; Mg,  $8.97 \times 10^{-12}$ ; Cl,  $14.5 \times 10^{-12}$ ; Ni,  $18.4 \times 10^{-12}$ ; Zn,  $53 \times 10^{-12}$ ; Br,  $20.4 \times 10^{-12}$ ; Hg,  $47 \times 10^{-12}$ . For ordinary *air*, the coefficient would be about  $62 \times 10^{-12}$ . The values for most of the even-numbered heavy elements (beginning with zinc) are doubtless high, like those for zinc and mercury. The values have been calculated chiefly from atomic weight and positive-ray analysis data;<sup>18</sup> in the case of mercury, the value has been calculated from the approximate relation  $P' = M/RT \cdot B$ , using the experimental value of the ordinary (diffusion) separation coefficient *B* obtained by Mulliken and Harkins. An important feature of the centrifugal separation coefficient which differentiates it from the *ordinary* sepa-

$$\Sigma x_a M_a^2 - M^2, \text{ since } \Sigma x_a M_a = M, \text{ and } \Sigma x_a = 1. \text{ Then } \Delta_p M = \frac{\Sigma(M_a^2 x_a) - M^2}{2RT}. \quad (v^2 - v_0^2) = P'(v^2 - v_0^2) \quad (28')$$

The *last* expression in the *text* for *P'* of Equation 28' readily reduces, on expansion, to the form just obtained. *P* and *P'* are related to *E* of Equation 7A and *E'* of Equation

$$7A' \text{ of the previous paper. } E = \frac{(M_1 - M_2)^2 x_1 x_2}{c M_1} = \frac{2RT}{c M_1} \cdot P = \frac{RT}{M_1} \cdot P, \text{ if } c=2; \text{ and}$$

$$E' = \frac{\Sigma x_a x_b (M_a - M_b)^2}{c M} = \frac{2RT}{c M} \cdot P' = \frac{RT}{M} \cdot P', \text{ if } c=2.$$

<sup>16</sup> For gravitational separation, the expression corresponding to Equation 28' is  $\Delta_p M = 2P', g \Delta h$ . (29')

<sup>17</sup> Similarly, *E* could have been obtained from *E'* as a special case, in the previous paper.

<sup>18</sup> The value for zinc is based on the existence of four isotopes 64, 66, 68, and 70, as recently reported by Dempster.

ration coefficient, is that it is *independent*<sup>19</sup> of the *state of combination* of the element,<sup>20</sup> and is thus characteristic of the latter. This is true for each element even in compounds containing more than one isotopic element.<sup>21</sup> The ordinary separation coefficient for a given element is in-

<sup>19</sup> If the molecules are built up from the atoms *according to chance*, the mol-fractions of the various *molecular* isotopes are given by the successive terms of the expansion of  $(x_1 + x_2 + \dots x_n)^{n_s}$ , where  $x_1, x_2, \dots$ , refer to the *atomic* isotopes (see the previous paper for derivation of this). On this basis, the exact constancy of  $P'/n_s$  has been tested by comparison of the algebraic expressions for  $n_s = 1, 2, 3$ , and 4, for a mixture of *two* isotopic atomic species, and by calculation of numerical examples for  $n_s = 1$  and 2, for the case of a mixture of *three* atomic isotopes. ( $P'$  is here the *molecular* separation coefficient,  $n_s$  the number of atoms of the element per molecule). Although no general proof has been obtained, it is probable that *all* possible expressions for  $P'/n_s$  for various compounds of an element containing any number of isotopes, can be *reduced* to a common expression, the same as that for the case  $n_s = 1$ . Mathematically, the relation  $P'/n_s = \frac{\Sigma(M_b^2 x_b) - M^2}{n_s} = \Sigma(A_a x_a) - A^2$  would have to hold for all compounds and all values of

$n_s$ . For a mixture of *two* isotopes, this reduces to  $(A_2 - A_1)^2 x_1 x_2$  ( $A$  and  $M$  stand for atomic and molecular weights respectively, and the subscripts  $a$  and  $b$  refer respectively to atomic and molecular species). The existence of this relation no doubt springs from an absence of dependence of the value of  $\Delta x_a$  (for any given *atomic* isotope in a given operation) on the manner of *distribution* of the atomic species  $a$  among the various *molecular* isotopes present. Apparently the assumed distribution, *i. e.*, according to chance, is such as always to yield the same result, so that the change of atomic weight,  $\Delta A = \Sigma(A_a - A_1) \Delta x_a$ , is independent of the particular compound in which the isotopic element occurs.

<sup>20</sup> Ordinarily the term "separation coefficient" is applied to the change of atomic weight of the *element* concerned. It could also be applied to the coefficients  $B, P$ , etc., for *molecules*, for the change of molecular weight. In the case of centrifugal separation, the molecular coefficient is equal to the sum of the products of the *atomic* coefficients by the numbers of atoms of the corresponding elements in the molecule.

<sup>21</sup> Suppose a compound of molecular weight  $M$  contains 2 or more isotopic elements. Let us divide  $M$  into 2 parts, such that  $M = X + Y$ . Let  $X$  stand for the partial molecular weight in the compound of the particular isotopic element which we are interested in.  $X$  will then be the atomic weight of this element times the number of atoms,  $n_s$ , which it contributes to each molecule. Let  $Y$  stand for the part of the molecular weight due to *all other* elements, some of which may be isotopic.  $M$  is really an *average* value for a large number of molecular isotopes;  $X$  and  $Y$  likewise are average values. The isotopes of  $M$  can be regarded as consisting of all possible combinations of the isotopic forms  $X_1, X_2$ , etc., of the partial molecule  $X$ , with the isotopic forms  $Y_1, Y_2$ , etc., of the partial molecule  $Y$ . The isotopes of  $M$  can then be designated by double subscripts, the first to denote the  $X$  isotope, the second to denote the  $Y$  isotope. Thus  $M_{21} = X_2 + Y_1$ . We may also wish to deal with an *average* value of  $Y$ , while considering the  $X$  isotopes individually, or *vice versa*. Thus let  $M_{20}$  represent  $X_2 + Y$ ;  $M_{02}$ ,  $X + Y_2$ , and so on.

Equation 28' shows no dependence of  $P'$  on the absolute value of  $M$ , so that if  $Y$  had only a single value (no isotopes), the (molecular) separation coefficient  $P'$  (see Ref. 20) corresponding to  $M$  would not be affected by the magnitude of  $Y$ , but would depend only on the isotopic composition of the partial molecule  $X$ . That is,  $P'$  would be the same whatever the value of  $Y$ , whether  $Y_1, Y_2$ , or some other value. If we consider the

versely proportional to the molecular weight of the compound in which it appears, but is otherwise independent of the state of combination<sup>22,23</sup> (i. e., of the number of its atoms per molecule or the presence of other isotopic elements). Due to this mass factor, the ordinary coefficient tends to fall with increasing atomic weight of the isotopic element (this tendency is largely balanced by the increasing spread of the atomic weights of the isotopes), whereas the centrifugal separation coefficient is not so affected. Centrifugal separation is therefore *relatively* much more favorable to the heavy elements, as well as *absolutely* due to the increased number of isotopes. The effect of the atomic weight differences and of the mol-fractions of  $X$  partial molecules collectively, they can be divided into several groups of identical composition, distinguished by being combined with different  $Y$ 's. Of all the molecules present, the fraction  $y_1$  will be in the group  $XY_1$ ,  $y_2$  in  $XY_2$ , etc. Since for every fraction by itself, the separation coefficient would have the value  $P'$ , the same must be true of the substance as a whole. That is, the value of  $P'$  is independent of the isotopic composition of the  $Y$  part of the molecule. The correctness of this result is not affected by the fact that the mol-fractions  $y_1$ ,  $y_2$ , etc., change during the diffusion due to the separation of the isotopes in the  $Y$  part of the molecular weight, for the reasoning above holds at *any instant*, whatever the relative proportions of the different  $Y$  groups (the coefficient  $P'$  is in its derivation an instantaneous quantity). The elementary coefficient  $P'/n_0$  has already been shown with reasonable certainty (Ref. 19) to be independent of  $n_0$ , so that is now shown to be altogether independent of the state of combination of the element. Thus separation proceeds, for each isotopic element in a mixed molecule, independently of the other elements present.

The discussion above can be put in a mathematical form which will be useful as a basis for Ref. 23. Suppose the separation coefficient  $P'$  for any  $Y$  group were not necessarily independent of the nature of the latter. Then the actual separation coefficient would be an *average* over all the different  $Y$  groups. Denoting by  $P'_1$ ,  $P'_2$ , etc., the several values of the separation coefficient corresponding to  $Y_1$ ,  $Y_2$ , etc., we would have  $P' = P'_1 y_1 + P'_2 y_2 + \dots = (1/2RT) [y_1 \Sigma x_a x_b (M_{a1} - M_{b1})^2 + y_2 \Sigma x_a x_b (M_{a2} - M_{b2})^2 + \dots]$ . But here  $M_{a1} - M_{b1} = M_{a2} - M_{b2} = X_a - X_b$ , that is, the effects of the different  $Y$ 's cancel, and the result is  $P' = \frac{\Sigma x_a x_b (X_a - X_b)^2}{2RT}$ , the same as if a single average value,

or the value zero, were used for  $Y$ ; at the same time it is seen that  $P'_1 = P'_2 = \dots$ .

<sup>22</sup> The discussion in Ref. 19 applies to the values of the *approximate* diffusion separation coefficient  $E'/n_0$  (which is proportional to  $P'/n_0$ ), except that  $E'/n_0$  is *inversely proportional to the total molecular weight*:  $E' = \frac{2RT}{c} \cdot \frac{P'}{M}$ . It also applies ap-

proximately to the exact coefficient  $B$  or  $B'/n_0$ , holding usually to within 1 or 2% for the latter. These relations were stated in the previous paper but not as fully discussed as here.

<sup>23</sup> In the case of the ordinary separation coefficient we have analogous to the above discussion in Note 21,  $E'/n_0 = \frac{1}{cn_0} \left[ \frac{y_1 \Sigma x_a x_b (X_a - X_b)^2}{M_{01}} + \frac{y_2 \Sigma x_a x_b (X_a - X_b)^2}{M_{02}} + \dots \right]$   
 $= \frac{\Sigma x_a x_b (X_a - X_b)^2}{cn_0} \left[ \frac{y_1}{M_{01}} + \frac{y_2}{M_{02}} + \dots \right] = \frac{\Sigma x_a x_b (X_a - X_b)^2}{cn_0 M}$ , nearly,  $= \frac{2RT}{cM} \cdot (P'/n_0)$ .

These relations of course hold also for  $E$  ( $n_0=1$ ), and for  $B$  and  $B'/n_0$ ; in all cases approximations are involved, but these are usually close.

the various isotopes of a given element, is the same for both the ordinary and the centrifugal separation coefficients (also for the thermal diffusion coefficient); they differ in the dependence of the former (the same is true of the thermal coefficient) on the magnitude of the atomic (or molecular) weight.

In a centrifugal separation, the degree of separation varies continuously with the distance from the axis of the apparatus, as expressed by Equation 28 or 28'. In using Equations 23 and 28 or 28' it should be remembered that  $\Delta_p M$  is the *difference* in atomic weight between material in different regions. The *absolute* atomic weights of any fractions depend on the *distribution* of material in the centrifuge. The only generalization which can be made is that the original or average atomic weight must be somewhere between the extremes at center and periphery. If the material were largely concentrated in the periphery, the decrease of atomic weight would be nearly  $\Delta_p M$  for the light fraction, while the increase would be only slight for the denser fraction. Note that  $\Delta_p M$  varies as the square of the angular velocity, and also as the square of the radius.  $\Delta_p M$  also varies inversely as the absolute temperature.

It is of interest to calculate the peripheral velocity  $v$  (or in general the value of  $\sqrt{v^2 - v_0^2}$ ) necessary to produce a difference of atomic weight  $\Delta_p M$  equal to that secured in an ordinary diffusion or evaporation with a cut of 2. For the latter case,  $\Delta \Delta M = 2B \ln 2$ ; for the former,  $\Delta_p M$

$= \frac{M}{RT} \cdot B \cdot v^2$ , nearly. Equating  $\Delta_p M$  and  $\Delta \Delta M$ , it is found that  $v^2 = \frac{1.386RT}{M}$ . This gives  $v = \frac{181,000}{\sqrt{M}}$  for  $t = 20^\circ\text{C}$ . For  $M = 6.94$  (Li),

$v = 6.9 \times 10^4$ ; for  $M = 36.46$  (HCl),  $v = 3.0 \times 10^4$ ; for  $M = 200.6$  (Hg),  $v = 1.28 \times 10^4$ . If the ratio of the value of  $\Delta_p M$  for  $v = 10^5$  to that of  $\Delta \Delta M$  for a cut of 2 is calculated the values obtained are, 2.2 for Li, 11.1 for HCl, 61 for Hg. If  $v = 10^4$ , the ratios are, 0.022, 0.111, and 0.61. The value of the centrifugal method evidently depends on the possibility of obtaining and using a velocity approaching  $10^5$  cm./sec. If this can be done, the centrifugal method is clearly superior in theory to any other method for the *heavier* elements. The method has additional superiority in the fact that the separation should be just as great for *any compound* of an element, as already pointed out. There are, however, a number of difficulties, especially for the heavier elements, aside from that of obtaining the necessary speed.

**Drawbacks to Centrifugal Method.**—Among the factors that reduce the apparent advantages of the application of the centrifugal method to the separation of gaseous isotopic mixtures are (1) the difficulty of constructing a centrifuge which could consistently turn out separated products

at as great a rate as a diffusion or evaporation apparatus; (2) the fact that the value of  $\Delta_p M$  depends on  $(v^2 - v_0^2)$ , not on  $v^2$  alone; (3) the necessity for removing the products continuously while the centrifuge is moving at full speed; (4) the fact that  $\Delta_p M$  represents the *extreme* separation, and that it will be difficult to design an apparatus, continuous or otherwise, that will separate the input material at all completely into two more or less equal extreme fractions, especially in view of the fact that (5) at high speed a gas will very largely condense to a liquid, or become highly compressed, close to the periphery, so that the light fraction will be extremely small. In connection with (4), the *average* value of  $\Delta_p M$ , referred to the composition at the point  $r_0$  nearest the center of the centrifuge, for the material between any two radial distances  $r_1$  and  $r_2$  from the center, is

$$(\Delta_p M)_{r_1}^{r_2} = \frac{\int_{r_1}^{r_2} (\Delta_p M) r dr}{r_2 - r_1} = \frac{P \omega^2 \int_{r_1}^{r_2} (r^2 - r_0^2) dr}{r_2 - r_1} = P \omega^2 \left[ \frac{(r_2^2 - r_1^2)/3 - r_0^2(r_2 - r_1)}{r_2 - r_1} \right] = \frac{1}{3} P \omega^2 (r_2^2 + r_1 r_2 + r_1^2 - 3r_0^2). \quad (30)$$

This is accurate only if the density is practically constant, and so is applicable especially to liquids. If the whole material is divided into two *equal* fractions by volume, then for a whirling cylindrical tube, or for a hollow disc, the actual separation, or difference in atomic weight, will be about *half* the *extreme*  $\Delta_p M$ . It can be shown that in such a case the departure of the *denser* fraction from the original or average composition is greater than that of the less dense fraction. If only extreme fractions are taken, the larger separation is at the expense of quantity. If the value of  $\Delta_p M$  is large, there will be a large density-gradient (Factor 5), which will again reduce the quantity of the light fraction. The *ratio of total pressure* from periphery to center can be calculated from Equation 26

$$\ln p/p_0 = \frac{M(v^2 - v_0^2)}{2RT} = \frac{M}{P} \cdot \frac{\Delta_p M}{2RT} = \frac{\Delta_p M}{2B}, \quad (31)$$

$P$  (or  $P'$ ) being given by Equation 28 or 28'. For  $\Delta_p M = 1.386 B = (\Delta \Delta M)_c = 2$ , we found  $v = \frac{181,000}{\sqrt{M}}$ , and so  $\ln p/p_0 = \frac{(181,000)^2}{2RT}$ , or  $p/p_0 = e^{0.687} = 2.0$ . This pressure ratio is not large, but neither are the values of  $\Delta_p M$ . For large values of  $\Delta_p M$ , where the centrifugal method would be really worth while, the pressure ratio becomes large, and the difficulty of obtaining any appreciable quantity of separated product is greatly increased. Thus for  $\Delta_p M = 13.86 B$ ,  $p/p_0 = (2)^{10} = 10^3$ . For the high pressure ratios, the concentration of material near the periphery will be even more marked, due to departure from the behavior of a perfect gas. These difficulties cannot well be avoided by any special method of design.—

Note that from (31),  $p/p_0 = e^{\Delta_p M/2B}$ . This means that insofar as the value of  $p/p_0$  sets a practical limit to  $\Delta_p M$ , the coefficient  $B$ , instead of  $P$ , is important, so that the heavy elements lose their advantage. On the whole, it seems probable that the direct separation of a gas or vapor into fractions by centrifuging would have no practical superiority, as a means of separating isotopes, over the diffusion or evaporation methods.

**Method of Evaporative Centrifuging.**—The following special adaptation of the centrifugal method seems rather promising as a means of securing a fairly large separation in a single operation in the case of certain gases. It should give greater separation than the method of dividing a gas directly into fractions, as well as being largely independent of the difficulties caused by large pressure ratios. For this purpose, the apparatus should have a considerable capacity near the periphery, which should be in free communication with the center, so that equilibration would be rapid. The gaseous isotopic mixture to be centrifuged would be admitted through a tube connected with the center of the centrifuge. As the latter speeded up, more and more gas would be drawn in, and compressed or condensed in the periphery. When equilibrium had been established, under conditions such that nearly all the gas was concentrated in the periphery, the gas would be drawn off very slowly by reducing its pressure at the center of the apparatus. Any desired cut could be made, and the process would be analogous in its results to, although entirely different in mechanism from, a process of irreversible evaporation having a *separation coefficient* equal to the value of  $\Delta_p M$ , which represents difference in atomic weight between center and periphery. Gas thus drawn off corresponds to the "instantaneous condensate" in an evaporation. For the *residue*, in the periphery, the increase in atomic weight would be

$$(\Delta M)_p = \Delta_p M \ln C = P v^2 \ln C; \quad (32)$$

for the gas drawn off,

$$(-\Delta M)_p = \frac{\Delta_p M \ln C}{C-1} = \frac{P v^2 \ln C}{C-1} \quad (33)$$

and the total difference in atomic weight between the two fractions would be

$$(\Delta \Delta M)_p = \frac{P v^2 C \ln C}{C-1}. \quad (34)$$

These equations are analogous to (7), (16), and (19). For a cut of 2,  $(\Delta \Delta M)_p = 1.386 P v^2$ . In this last case, two *separated fractions* differing by  $1.386 P v^2$  would be obtained; whereas, by merely splitting the gas in a centrifuge at the same speed into two fractions, even if the density of the gas could be uniform, the difference in average composition of the two fractions would be only  $P v^2/2$  units of atomic weight. The modified method thus should give a much larger practical separation, even aside from the question of the pressure ratio effect. Further, the product can be taken

off in several fractions, if desired, and a large cut can be made on the residue in one operation, greatly increasing the separation. The method thus strongly resembles the evaporation method, and may be called "evaporative centrifuging." In practice, the efficiency of the method will be reduced somewhat (1) by the very fact that not all the gas will be in the periphery initially, and (2) by the disturbance of equilibrium caused by the drawing off of the gas. For the successful operation of the method of evaporative centrifuging, the speed and quantity of material used must be so adjusted that the gas pressure at the center will be great enough to handle, while the material in the periphery is, preferably, in the liquid state. This condition can be fulfilled, up to fairly high peripheral velocities, by a few gases of high critical pressure and low boiling point, such as hydrogen chloride, bromide, selenide, telluride and silicide. Thus for hydrogen chloride at  $v = 10^5$ ,  $(\Delta\Delta M)_p$ , for a cut of 2, would be 15 times as great as  $\Delta\Delta M$  for a diffusion or evaporation. If the hydrogen chloride behaved like a perfect gas, the pressure ratio (about 2200) would correspond to a range from 15 mm. to 45 atmospheres, the latter being approximately the vapor pressure of hydrogen chloride at  $20^\circ$  (the *critical* pressure is 86 atmospheres).

**General Considerations Respecting the Centrifuging of a Gas.**—For the lightest elements, the centrifugal method has no great theoretical superiority over the diffusion methods in degree of separation even for  $v = 10^5$ . For the *heavier* elements or *compounds*, the *pressure ratio* becomes excessive at velocities too low to yield a very great separation. For gases of *low critical pressure*, the pressure ratio again limits the separation. For liquids, or gases of high critical temperature, *heating* is required (note that the degree of separation is inversely proportional to the absolute temperature). Thus the method of evaporative centrifuging is restricted in its usefulness to some of the elements of medium atomic weight. Here a separation 10–15 times as great as that obtainable by diffusion methods can be hoped for in a single operation. A greater separation than this in a single operation can hardly be hoped for under any practicable conditions.

**Factors of Importance in Separating Isotopes by the Centrifuging of a Liquid.**—As far as theory is concerned, a very large separation might be expected in the centrifuging of *liquid* elements of high atomic weight. One great advantage of such a method would be the ease with which the material could be divided into fractions, the difficulties caused by compression and condensation in the case of gases at high pressure ratios being practically absent. Equation 30 would apply quite well to the fractions obtained in centrifuging a liquid. New difficulties, however, enter if one attempts to obtain the largest separations. Thus for  $v = 10^5$  cm. per sec.,  $\Delta_p M$  is 60 times as great for mercury as is  $\Delta\Delta M$  for a cut

of 2 by a diffusion; *but* under these conditions the calculated pressure in the peripheral portion of the centrifuge would be 70,000 atmospheres,<sup>24</sup> and it is found that the degree of separation is directly proportional to the peripheral pressure. Thus this factor involves enormous, if not insuperable difficulties of construction for very large separations. The use of a suitable liquid compound of a heavy element of lower density would of course improve matters; and the use of an aqueous solution of a salt has possibilities (several difficulties might come up here; also, the *capacity* of the apparatus would be greatly reduced). The most important practical difficulty, as is shown by experimental evidence given below, is the effect of even slight vibration in nullifying the tendency toward separation.<sup>25</sup> This may or may not be insuperable. Another practical factor to be considered is the rate of attainment of equilibrium, but the conditions are favorable in this respect. The evidence for the correctness of the *theory* in the case of a liquid seems practically as conclusive as for the case of a gas.

**Theory of Separation of Isotopes by Liquid Centrifuging.**—Lindemann and Aston<sup>11</sup> give for the separation of a liquid into isotopes by centrifuging the same equation as for a gas. In connection with a discussion of the possibility of separating liquid mercury by this method, Poole<sup>26</sup> gives a detailed derivation which would lead to equations identical with those of Lindemann and Aston, although Poole does not make the necessary final step. The equations in the present paper would then also hold. In Poole's derivation, he assumes that the buoyancy effect caused by the relative centrifugal force on the assumed two isotopes, which have equal atomic volumes, is balanced by the "osmotic pressure" which is set equal to  $cRT$ .

The problem can be attacked from another point of view. Suppose an isotopic liquid and its saturated vapor to be centrifuged side by side in a tube, the two phases being separated by a longitudinal membrane permeable only to the vapor.<sup>27</sup> Let enough time be allowed for the at-

$$^{24} \text{ In general, the peripheral pressure } P_r = \int_{r_0}^r dP =$$

$$\int \frac{\rho v^2 dr}{r} = \int \rho \omega^2 r dr = \frac{\rho \omega^2 (r^2 - r_0^2)}{2} = \frac{\rho (v^2 - v_0^2)}{2}$$

if  $\rho$ , the density, is assumed constant, or an average value taken. Since  $\Delta_r M$  is also proportional to  $(v^2 - v_0^2)$ , the peripheral pressure is evidently directly proportional to the degree of separation obtained.

<sup>25</sup> It seems unlikely that this effect could interfere seriously with the method of evaporative centrifuging of a gas, already discussed.

<sup>26</sup> Poole, *Phil. Mag.*, [6] 41, 818 (1921).

<sup>27</sup> The vapor would of course be highly supersaturated and would tend to condense in the free vapor space at the peripheral end of the tube, thus leading to a distillation of the confined liquid until it was equally distributed on both sides of the membrane.



tainment of a steady state. By the familiar type of proof based on the second law of thermodynamics, the (*total*) vapor pressure at every point must be that corresponding to equilibrium with the liquid under (centrifugal) pressure in the other tube.<sup>28</sup> Now suppose the equilibrium composition-distribution were not the same in both tubes, when allowed to reach equilibrium independently. Then there could not be composition equilibrium between the two phases across the membrane, when the other equilibria were satisfied. As a result of the conflicting equilibrium conditions, a perpetual circulation of the isotopes would go on (the denser ones in one direction, the less dense in the opposite, presumably). No equilibrium could be attained in either phase, and the system would be capable of doing work continuously at constant temperature at the expense of thermal energy. This would violate the second law of thermodynamics, and the statistical mechanical principles underlying it. We may then conclude that the isotopic composition will be identical at corresponding points in the two tubes. The equations previously obtained for an ideal gas are then applicable to any liquid whose saturated vapor behaves like an ideal gas, and undoubtedly also, by the principle of continuity, to *any* liquid or compressed gas whatever.

**Experimental Work on the Separation of Isotopes by Liquid Centrifuging.**—An unsuccessful attempt was made by Joly and Poole<sup>29</sup> to detect a separation of the isotopes of lead after centrifuging ordinary lead in the liquid state in steel tubes, with a peripheral velocity of  $10^4$  cm./sec. The expected separation was, however, within the limit of error of the density determinations. They secured, nevertheless, a decided separation in the case of certain alloys. Poole<sup>26</sup> later discussed the possibility of securing a separation with mercury, but concluded that the separation (30 parts per million in density) to be expected with their centrifuge would be too small to measure. Actually, much smaller changes in the density of mercury can be determined, as has been shown by Brönsted and Hevesy<sup>30</sup> and especially by Mulliken and Harkins.<sup>3</sup> With the idea of testing the theory experimentally, two steel tubes were made to fit a large laboratory centrifuge. Thick-walled glass tubes were first tried, but their capacity was small and breakage too frequent. A speed of about 2300 r.p.m. was attained. The inner end of each tube was 7.1 cm. from the center of the centrifuge, the outer end 26.3 cm. The tubes held 13 cc. each. The calculated extreme separation is  $(\Delta_p M) = 8.8$  parts. This tendency, however, does not in the least invalidate the argument. It has no bearing on the equilibrium between the vapor and confined liquid at any point.

<sup>28</sup> As far as the *total* vapor pressure is concerned, the *isotopic composition* of liquid or vapor should be a matter of indifference, since all the evidence shows that the vapor pressures of isotopes are practically, if not exactly, equal.

<sup>29</sup> Joly and Poole, *Phil. Mag.*, [6] 39, 372 (1920).

<sup>30</sup> Brönsted and Hevesy, *Phil. Mag.*, [6] 43, 31 (1922).

per million in density. The centrifuged material was divided into thirds, and the densities of the inner and outer thirds compared. The expected difference was about  $\frac{2}{3} \times 8.8 = 5.9$  p.p.m. (by Equation 30). This is very much greater than the experimental error in the density determinations. The results were conclusively negative to within 0.5 p.p.m. in each of three runs (a 40-minute run with glass tubes, and two 8-hour runs with the steel tubes). In the first of the latter runs there was a little vibration, but great care was taken in the second run to reduce this to a minimum by adjusting the weights of the tubes (these were somewhat unequal for the best balancing). There was still detectable vibration, however, which increased after the run had started. The pycnometer weighings,<sup>31</sup> each corresponding to a separate refilling of the pycnometer, were made and corrected as described in the previous paper. They are all reproduced in Table I to show the conclusiveness of the results and to illustrate the accuracy of the density comparisons. In Run 1, the pycnometer used contained about 96 g. of mercury, in the other runs, 107 g.

TABLE I

Run	Time Hours	Corrected weight of filled pycnometer		
		Uncentrifuged	"Heavy" Fraction	"Light" Fraction
1	$\frac{2}{3}$	.....	116.32900	116.32900
			116.32885	116.32897
			Av. 116.32893	Av. 116.32899
2	7.5	124.09339 124.09341 ..... Av. 124.09340	124.09343	124.09339
			(124.09321)	124.09338
			124.09336	
			Av. 124.09340	Av. 124.09339
3	8	.....	124.09393	(124.09431)
			124.09398	(124.09355)
				(124.09379)
				124.09391
				124.09400
				124.09397
			Av. 124.09396	Av. 124.09396

It was suspected that vibration was the cause of failure to obtain a separation. The process of establishment of the equilibrium state under centrifugal force is one of diffusion,<sup>32</sup> so that the rate of diffusion is also an

<sup>31</sup> None of the weighings made has been omitted in the table. In taking averages, those in parentheses have been rejected. This is justified by the close agreement of the remaining values, as well as by other evidence (pump not working properly) in the case of the two low values for Sample 3. Low values are usually due to incomplete filling and are very likely to be wrong when consistent higher values are obtained. Uncommonly high values are usually due to an unnoticed minute drop of mercury on the outside of the pycnometer.

<sup>32</sup> This factor is discussed in an article (of which only an abstract was available to the writer) by von Hevesy, *Verh. Deutschen. Physik. Ges.*, 1, 47 (1920), in connection with a discussion of Joly and Poole's attempt (Ref. 29) to separate the lead isotopes. Von Hevesy also discusses the case of an aqueous solution of a lead salt.

important factor. We may reasonably assume that the separation of the isotopes would take place at the same rate under centrifugal force as return to uniformity of composition would occur after the stopping of the centrifuge. We may assume  $2.0 \text{ g./cm.}^3/\text{day}$  as a reasonable value for the autogenic diffusion of mercury. Then for a tube 20 cm. long, if the difference of density at the two ends has *any* value  $\Delta d$ , we can obtain an idea of the rate of diffusion by assuming a uniform density gradient equal to  $\Delta d/20$ . On this basis, it is found, assuming mercury to consist of a mixture of two isotopes differing by 3 units in atomic weight, that in 24 hours enough of the heavy isotopes would pass from one-half of the tube to the other to neutralize the initial gradient five times over, if the latter were maintained constant. From this rough calculation, it is evident that in 8 hours composition equilibrium under centrifugal force should be approached.

The effect of vibration and of diffusion-rate were directly tested, as follows. The lower half of each steel centrifuge tube was filled with some mercury having a density 12 p.p.m. greater (weight of filled pycnometer 124.09526 g.) than that of ordinary mercury (weight of filled pycnometer 124.09401 g.), which was used to fill the upper half of each tube. The tubes were then centrifuged at full speed for  $1\frac{1}{2}$  hour, there being slight vibration during the operation. The densities of the material in the two halves of the tube were now redetermined, and found practically identical (lower half,  $W = 124.09466$ , upper half,  $W = 124.09461$ ). The tubes were then refilled in the same way with fresh material and allowed to stand quietly for the same total time as before (53 minutes). This time, the material of the lower half showed a decrease of density of only 0.15 mg. ( $W = 124.09511$ .) Finally, the same fractions were returned to the tubes which were then allowed to stand undisturbed for  $8\frac{1}{2}$  hours. Diffusion was now nearly complete.<sup>33</sup> ( $W = 124.09475$  for the material from the lower end of the tube; decrease = 0.51 mg. out of a possible 0.63 mg.)

**Conclusions in Regard to Liquid Centrifuging.**—The above results give direct proof that diffusion is sufficiently rapid to permit separation, but that vibration of the centrifuge is sufficient to prevent it (the effect of vibration would of course be less if diffusion were more rapid). The result shows that on account of the latter factor, the separation of isotopes by the centrifuging of a liquid is not a promising method, although it might be possible in a very accurately, heavily constructed and perfectly balanced centrifuge. The results do not, of course, give any evidence as

<sup>33</sup> Experiments of this sort can be used to determine the autogenic diffusion coefficient of mercury, somewhat as Gróh and von Hevesy [*Ann. Physik*, [4] 63, 85 (1920)] used a radioactive isotope to determine the corresponding coefficient in the case of lead.

to the validity of the theory of centrifugal separation. The theoretical evidence for this, however, seems conclusive.

### Summary

1. The theory of the separation of isotopes by thermal diffusion and by centrifuging is discussed. Equations are developed giving the difference in atomic weight obtainable in any operation, similar to the equations for diffusion and evaporation processes obtained in a previous paper.<sup>2</sup>

2. For thermal diffusion, the difference in atomic weight between portions of an isotopic gas at temperatures  $T_1$  and  $T_2$ , respectively is  $\Delta_i M = K \times B \ln T_1/T_2$ , approximately, the atomic weight being greater at the colder end.  $B$  is the ordinary separation coefficient as defined in the previous paper.  $K$  is an approximate constant for each element, having a value probably near  $1/4$ , and depending on the behavior of the molecule during impacts. The term  $KB$  may be called the thermal separation coefficient. The method of thermal diffusion is shown to be much less effective as a means of separating isotopes than ordinary diffusion or evaporation. A somewhat more advantageous modification of the method is described under the name of evaporative thermal diffusion.

3. For the centrifuging of a gas the difference in atomic weight between the central and peripheral regions is  $\Delta_i M = P(v^2 - v_0^2)$ , where  $P$ , the "centrifugal separation coefficient," is a characteristic constant for each element ( $v$  and  $v_0$  denote velocities at the peripheral and central regions of the material under treatment). Values of  $P$  for various elements are given. It is shown that the value of  $P$  is unaffected by the state of combination of the element, even if the compound contains other isotopic elements. Thus the separation is equally great for all compounds of a given element. This is in contrast to the situation with all the other diffusion methods, for which the degree of separation of a given element in one operation is inversely proportional to the molecular weight of the compound. Further, the value of  $P$  for any element is independent of the atomic weight, while the ordinary separation coefficient  $B$  is inversely proportional to the latter. Hence, the theory is on this basis relatively increasingly more favorable to the centrifugal method as the atomic weight increases.  $P$  is equal to  $\frac{(M_2 - M_1)^2 x_1 x_2}{2RT}$  for a mixture of two isotopes, and for a mixture of several isotopes is given by  $\frac{\sum_a \sum_b x_a x_b (M_a - M_b)^2}{2RT}$ .  $P$ , unlike  $B$ , is inversely proportional to  $T$ , but

depends on the atomic or molecular weight intervals  $(M_a - M_b)$  and mol-fractions ( $x$ 's) in the same way as  $B$ .

4. Although for the heavy elements the theory predicts, for a peripheral velocity of  $10^5$  cm./sec. a separation many times that obtainable

in a single diffusion or evaporation, it is shown that compression and condensation of the gas or vapor into the peripheral region make such large separations impracticable if carried out in any ordinary way. The pressure ratio between the two regions is given by  $\frac{\ln p}{p_0} = \frac{M}{P} \cdot \frac{\Delta_p M}{2RT}$  (strictly true only for an ideal gas), and so increases with atomic and molecular weight.

5. A special method which is called "evaporative centrifuging" is proposed whereby gas condensed in the periphery of the centrifuge at high speed would be allowed to evaporate very slowly, the light fraction being drawn off gradually at low pressure from the center of the apparatus. The process would be in effect precisely analogous to an evaporation in which the separation coefficient was increased from  $B$  to  $Pv^2$ . This method, applicable at room temperature to hydrogen chloride, bromide, selenide, telluride and silicide, and perhaps to other substances, though less advantageously, with heating, might be expected with peripheral velocities up to  $10^5$ , to yield a separation 10 or 15 times as great in a single operation as would an ordinary diffusion or evaporation. No serious objection to the method is obvious. The method may be the most rapid method of separating isotopes for some of the elements of medium atomic weight, provided a suitable centrifuge of reasonable capacity and the necessary speed can be constructed. For the lighter or heavier elements, the method is less promising.

6. The theory of the separation of isotopes by the centrifuging of a liquid is discussed, and a thermodynamic demonstration given that the degree of separation for a given apparatus is identical for liquids, gases, and intermediate states of matter. An account is given of an attempt to test the theory in the case of liquid mercury. The conclusively negative results obtained are shown by an experiment to be attributable to a slight vibration of the centrifuge. This effect is likely to prove a limiting factor in any attempt to use the theoretically very promising method of liquid centrifuging. The effect of other factors is discussed, including that of diffusion rate. The latter is shown theoretically, and experimentally by determining the rate of interdiffusion of separated isotopes, to be sufficiently great in the case of mercury (and undoubtedly in general), to permit an approach to the theoretical equilibrium state of partial separation in a few hours.

7. The above discussion applies to the separation by centrifuging of non-isotopic gases of nearly equal molecular weight (e. g., air), and also of ideal solutions. The chief difficulty in the case of the latter would be the effect of vibration.

8. Some equations and discussions applicable to the previous paper are given, viz., Equations 19 and 19A, and References 17, 20, 22, and 34.

In particular, a demonstration is given of the at least approximate independence of the ordinary separation coefficient, for any element, of anything but the total molecular weight, even if the molecule contains other isotopic elements. Examples are also given in Table I of the extreme accuracy of the density comparisons which can be made with the pycnometer described in the previous paper.

It may be well to correct here certain conclusions given in the previous paper (pp. 40-41) in regard to the rate of separation of isotopes by gaseous diffusion, *i. e.*, diffusion of an isotopic gas through a thin layer of another gas enclosed in the pores of a membrane. Briefly, this method is now found to be always *less* favorable than molecular diffusion, instead of *more* favorable, as previously concluded. This is due to the effect of the increased mean free path of the heavier molecules which results from persistence of velocity. This factor was expressly neglected before. Further, it now appears that mass motion, either positive or negative, should have practically no effect on the rate of separation, except indirectly as it may affect back pressure and so efficiency. A fuller discussion of this subject will be given later. Experimental work is now being carried on with mercury.

Acknowledgment should have been expressed in the previous paper of indebtedness to the C. M. Warren Fund of the American Academy of Arts and Sciences for a grant of five hundred dollars made to Professor William D. Harkins. A part of this grant was used in the purchase of an extremely accurate balance which was available for use in the previous investigation on the separation of the isotopes of mercury by the evaporation method, as well as in the present work.

CHICAGO, ILLINOIS

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[CONTRIBUTION FROM THE WOLCOTT GIBBS MEMORIAL LABORATORY, HARVARD UNIVERSITY]

## THE HEAT OF SOLUTION OF ZINC IN HYDROCHLORIC ACID

By THEODORE W. RICHARDS AND THORBERGUR THORVALDSON

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The heats of solution of metals in acids—data which are the basis of the computation of the heats of formation of all compounds of metals—are worthy of especial attention. The incompleteness of Thomsen's method of correcting his results for the heat of dilution of the solutions employed<sup>1</sup> and the merely approximate character of early work renders revision desirable.

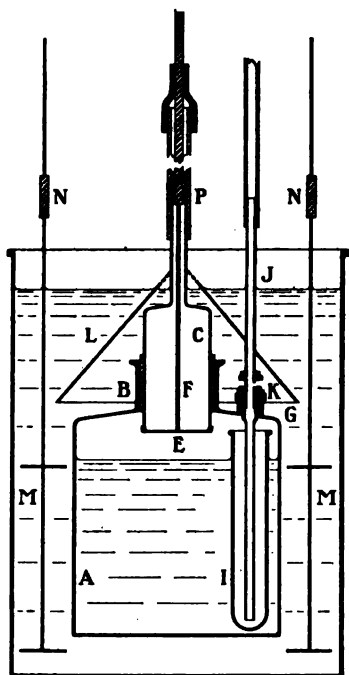
Revision was, indeed, begun over a decade ago. Values for the heat of solution of zinc, aluminum, magnesium, cadmium and iron in hydrochloric acid were found which in some cases differed markedly from Thomsen's

<sup>1</sup> Richards and Burgess, *THIS JOURNAL*, 32, 431 (1910).

values.<sup>2</sup> This research was, however, preliminary in character. As was duly indicated, the needful corrections for the heats of dilution of the solutions were sometimes so large as to cause uncertainty. The present communication presents a repetition of the experiments with zinc under better conditions. The new results substantiate the old ones within a reasonable limit of error but are, nevertheless, so much more satisfactory that it is worth while to recount them in detail. The experimental work was finished in 1914, but as usual the publication has been delayed.

**Apparatus.**—Since the chief difficulty in the preliminary work lay in the large volume of acid employed for dissolving the zinc, a new arrangement was devised which permitted the use of a much smaller amount of acid, thus greatly diminishing the error which might arise from the corrections due to the heat of dilution. In order that a relatively large

amount of zinc should be dissolved in this small amount of acid, without causing undue rise of temperature with its attendant complications, a large heat capacity was provided by immersing the reaction vessel in a large calorimeter filled with water. The whole was surrounded by an environment which could be changed in temperature so as to assure adiabatic conditions. The outer parts of the apparatus, including the 1.4-liter platinum calorimeter can, were identical with those used in the preliminary work, but the reaction vessel should be described in detail.



The Inner Calorimetric Vessel and Appurtenances.

This vessel was enclosed (with surrounding air space) in a water-tight envelope with tubes above. The envelope was immersed in a large bath, which was always kept at the same temperature as the inner vessel.

This reaction vessel consisted of a bottle (200 cc. in volume) of pure gold (A in the diagram) with two outlets above (B, G). The gold stopper (C) in the wider central outlet was made tight by a rubber band and contained, below, a movable inverted cap (E) for holding the zinc, which was thus kept within the bell-shaped stopper until the moment of beginning the experiment. At this moment the cap was lowered into the acid in the gold bottle and used as a stirrer.

In order to eliminate spray, the evolved hydrogen was caused to pass out of the bottle by a circuitous route, downward into a gold test-tube (I) contained within the bottle and then upward through a fine platinum side

<sup>2</sup> Richards, Rowe and Burgess, *THIS JOURNAL*, 32, 1176 (1910).

tube reaching almost to the bottom of the test-tube within the bottle. This test-tube also served to prevent reflux water from mixing with the contents of the bottle. The hydrogen afterwards emerged through water in the outer can, giving up its surplus heat and becoming saturated with water vapor. The screw stopcock (K) could, by turning, be closed at the start and conclusion of the experiment, being operated by a hard rubber tube attached to the platinum tube (J). The rubber tube (which projected from the top of the calorimeter jacket) could be closed above. An unsymmetrical cone of platinum foil (L), the apex of which reached a little above the surface of the liquid in the calorimeter, prevented the bubbles from spattering liquid upon the cover of the calorimeter. The stirring of the water in the main calorimeter was effected by a vertically reciprocating 2-stage stirrer of the conventional type, made of pure silver. This also, like the outside connection of the gold stopper and the platinum side tube, was thermally insulated by means of hard rubber. The assemblage is suitable, with minor modifications, for determining a great variety of thermochemical values, especially such as involve the absence of water in the reacting vessel.

The apparatus used for determining specific heats and heats of dilution has already been described in full in the earlier papers of this series.

All parts of each of these assemblages were individually weighed for the computation of the heat capacities.

The Beckmann thermometer employed had been carefully standardized in a variety of ways. The standardization finally accepted was that kindly carried out by O. C. Bridgeman and confirmed calorimetrically by S. Tamaru.<sup>3</sup> A thermometer of similar construction was used in the outside bath and one reading to  $0.1^\circ$  for the determination of the room temperature.

All temperature readings and all corrections were made to  $0.0001^\circ$ , and the result was then rounded off to the nearest thousandth. Hence, as far as possible, no single value should be more than  $0.0005^\circ$  in error.

The *averages* of many readings should be still better. Of course this limit of error applies only to the readings; it does not apply to any possible unknown constant error.

**Materials.**—Two samples of zinc were used in this work. One was the "reagent zinc," identical with that used earlier,<sup>1</sup> and found to give results identical with those from the most carefully purified electrolytic zinc. This specimen had been carefully analyzed and found to contain no amounts of impurity which could affect the present results. The second sample, B, was guaranteed "the purest zinc for analysis" and was found to be even purer than Sample A. The granules of metal were hammered into thin sheets, using a brightly polished hammer and anvil of the best tool steel. The trace of iron thus introduced could not have produced any essential effect on the thermochemical result. The thin sheets of zinc were kept in the desiccator over caustic alkali until needed. Hydrochloric acid was prepared from the purest acid of commerce by dilution with an equal amount of distilled water and distillation in a quartz container. The second third of the distillate was collected and made up exactly to the required strength,  $\text{HCl} \cdot 20\text{H}_2\text{O}$ . The final determination of the exact concentration was made by duplicate gravimetric silver chloride analyses. All quantities of materials were

<sup>3</sup> Richards and Tamaru, *THIS JOURNAL*, 42, 1376 (1920).



measured with weights compared with the international standard, and were reduced to that standard, as well as corrected to vacuum.

The knowledge of several specific heats was needed for the calculation of the results. The specific heat of  $\text{HCl} \cdot 20\text{H}_2\text{O}$  had previously been found to be 0.849.<sup>4</sup> By means of the apparatus employed in determining this datum, it was found that the specific heat of the solution remaining after the reaction of zinc on hydrochloric acid was 1.62% greater than that of the acid given above; this specific heat was therefore taken as 0.863. The specific heats of zinc, platinum, gold and silver were taken, respectively, as 0.092, 0.0324, 0.0312, and 0.055, while that of rubber was taken as 0.48. The specific heat of water was taken as 1.000 at 18° because the heat capacities were determined over the range 16° to 20°. Afterwards, all the results were reduced to 20°, using the 20° calorie.

### Details of Experimentation

The requisite amount of water was weighed in the platinum calorimeter vessel, and of  $\text{HCl} \cdot 20\text{H}_2\text{O}$  in the gold bottle, the gold test-tube and the connecting platinum tubes having been placed in position. The gold stopper (filled with a suitable weighed quantity of zinc, and with its trap-door below closed) was then fitted very tightly into the gold bottle, the screw valve (K) was closed, and the whole assemblage lowered into the calorimeter to a suitable depth, as indicated in the diagram. The bottle was held in position by means of the stout hard rubber extension (P) attached to the stopper. When the system had adjusted itself to a constant thermal condition, as indicated by the very slight regular change in thermometric reading produced by stirring, the trap-door cap (E) at the bottom of the stopper was pushed down (without breaking the air-tight joint above) thus immersing the zinc in the acid. By turning the side tube (J) after closing the valve at its top, the outlet at (K) was opened, and the hydrogen evolved was forced through the water. The bubbles, striking against the sheath afforded by the platinum cone, rolled up the inside of its surface and broke inside the cone. The gas escaping through small perforations in the platinum foil caused but very little spray. As long as the tubes (P) and (J) were closed at the top there was an excess of pressure of hydrogen within the gold bottle. Even if this, through leakage, was momentarily relieved, the gold test-tube acted as a trap to prevent water from mixing with the acid, thus yielding accidental heat of dilution.

When the solution of zinc was almost complete, as shown by the greatly diminished rate of temperature-rise, the outlet (K) was closed, and the valve at the top of P opened, the last trace of hydrogen being allowed to escape under atmospheric pressure into the air. The liquid within the gold bottle was then stirred by means of the lowered trap-door, until uniform

<sup>4</sup> Richards and Rowe, *THIS JOURNAL*, **42**, 1628 (1920).

temperature was obtained throughout. On dismantling the apparatus the water in the calorimeter was in each case tested to discover if any acid had found its way out of the gold bottle, but none was ever found. The gold test-tube never contained more than a few drops of liquid except in early cases of faulty manipulation. The whole with its contents was weighed after each determination in order to make sure that no water had entered from outside.

### The Heat of Solution of Zinc in Concentrated Hydrochloric Acid

Two preliminary series, of a few experiments each, were made by dissolving small amounts of zinc in acid in the apparatus thus assembled. They gave, within a reasonable limit of error, essentially the same result as the final series but, having less weight and adding little to the outcome, they were hardly worth publication. They served to perfect the details of experimentation and also, by their agreement, showed that no gross mistake had been made in any case.

The final series was much more trustworthy than the earlier ones and covered a greater range of temperature. Every experiment of this final series is included in the table below. For each, 9.000 g. of zinc was taken, and 170.00 g. of  $\text{HCl} \cdot 20\text{H}_2\text{O}$  was placed in the inner flask, quantities having the ratio  $\text{Zn} : 3.1116 \text{ HCl} \cdot 20\text{H}_2\text{O}$ . This flask was surrounded by 934.3 g. of water. The sum of these three heat capacities is 1079.4. From this must be subtracted 0.5, half the heat capacity of the moist hydrogen evolved, which should have been heated instead of being allowed to escape,<sup>5</sup> if the method of calculating the thermal result is rigorously applied. Finally, of course, the heat capacity 20.50 of the apparatus must be added. This latter quantity was made up as follows: platinum parts, 6.48; gold parts, 5.92; silver stirrer, 3.86; rubber, 0.81; thermometer, 3.42. Thus the total heat capacity of the system was taken as 1099.5 cal.(18°)/t.

The experiment, which lasted about half an hour, was conducted by the usual adiabatic method. The rise of temperature was so slow that the experimenter could keep the temperature of the environment very close to that of the inner vessel; it was always kept  $0.01^\circ$  or  $0.02^\circ$  above that of the calorimeter proper.<sup>6</sup> The outlets admitting the stirrer-shafts were duly plugged with cotton wool to prevent evaporation. If any cooling from this source took place, it must have been accounted for in the stirring correction, which was carefully determined before and after the experiment. Because of the length of time and of the necessity of preventing thermal stratification in the calorimeter, this correction was large, but in the series

<sup>5</sup> The first bubble was not heated at all; the last was evolved at the final temperature. Hence the correction is half the total heat capacity of the moist hydrogen under constant pressure.

<sup>6</sup> Ref. 1, p. 449.

given, it was possibly known within  $0.001^\circ$  and almost certainly within  $0.002^\circ$ . Therefore it did not introduce a serious disturbing element. The designations  $t_1$  and  $t_2$  in the table below are respectively the initial and final thermometer readings corrected to the standard of the platinum resistance thermometer. The correction (never more than  $0.002^\circ$ ) for the temperature of the exposed stem of the thermometer is entered with the stirring correction. The eight determinations of the final series showed a maximum range of  $0.003^\circ$  on each side of the mean.

TABLE I  
SOLUTION OF 9.000 G. OF ZINC IN EXCESS OF  $\text{HCl} \cdot 20\text{H}_2\text{O}$  (170.00 G.)

Expt.	Sample zinc	$t_1$ °C.	°C.	$t_2 - t_1$ °C.	Correction for stirring and stem °C.	Corrected rise of temperature °C.
1	B	16.034	20.161	4.127	-0.022	4.105
2	B	16.943	20.073	4.130	-0.026	4.104
3	B	16.946	20.076	4.130	-0.023	4.107
4	A	16.957	20.082	4.125	-0.018	4.107
5	A	16.989	20.108	4.119	-0.018	4.101
6	B	16.967	20.084	4.117	-0.012	4.105
7	A	16.943	20.069	4.126	-0.024	4.102
8	B	16.936	20.050	4.114	-0.012	4.102
						4.104

The heat capacity of  $1099.5 \text{ Cal.}(18^\circ)/t^\circ$  was evidently heated through  $4.104^\circ$ , and the heat thus measured was  $4512.4 \text{ Cal.}(18^\circ)$ . In terms of  $\text{Cal.}(20^\circ)$  this is  $4514.4$ .

For a gram atom the heat of this reaction of zinc on  $\text{HCl} \cdot 20\text{H}_2\text{O}$  (56% in excess) was  $32.789 \text{ Cal.}(20^\circ)$ , or  $137.06 \text{ KJ.}$ , if one  $\text{Cal.}(20^\circ) = 4.180 \text{ KJ.}$  Since the heat capacities of the factors were used, the result is the isothermal heat of reaction at  $20.09^\circ$ , the average final temperature.

The temperature coefficient of this reaction is easily computed, since the Kirchhoff rule applies to heats of reaction as well as to total energy changes, if consistently used. The increase of the total heat capacity during the reaction (conducted isothermally) is found from increase of heat capacity of the contents of the inner flask, as follows.

$$\begin{aligned}
 \text{Heat capacity of acid and zinc} &= 170.00 \times 0.849 + 0.81 = 145.14 \\
 \text{Heat capacity of zinc sol. and (moist gas) } p &= 178.68 \times 0.863 + 1.10 = 155.30 \\
 \text{Gain} &= 10.16
 \end{aligned}$$

The very striking increase,  $10.16$ , or about  $7\%$ , represents the gain of heat capacity which occurred when  $9.000 \text{ g.}$  of zinc (or  $1/7.2633$  gram atom) was dissolved. For a gram atom of zinc the corresponding amount is  $74 \text{ cal. } t$  which (with negative sign) equals the temperature coefficient of the reaction. Thus at  $20^\circ$  the heat evolved under the above conditions would be  $32.795 \text{ Cal.}(20^\circ)$ .

## Heats of Dilution of Factors and Products

Since the heat of the reaction  $\text{Zn} + 2\text{HCl} \cdot 200\text{H}_2\text{O} = \text{ZnCl}_2 \cdot 400\text{H}_2\text{O} + \text{H}_2$  was desired, it was necessary to determine the heats of dilution of the more concentrated acid used for dissolving the zinc as well as the heat of dilution of the product.<sup>7</sup> These heats of dilution were determined in apparatus which has already been described in full.<sup>8</sup> The combination designated *Ab* was used, and as arranged in these experiments, the apparatus had a heat capacity of 15.06 cal./t units. In each experiment 125.00 g. of solution was employed. The results for the respective rises of temperature follow.

TABLE II  
DILUTION OF HYDROCHLORIC ACID

No.	$t_1$ °C.	$t_2$ °C.	Stirring correction °C.	$t_2 - t_1$ corrected °C.
1	19.896	20.054	-0.006	0.152
2	19.898	20.057	-0.007	0.152
3	19.809	20.963	-0.001	0.153
4	19.736	20.890	-0.001	0.153
5	19.750	20.903	-0.001	0.152
6	19.729	20.882	-0.001	0.152
7	19.726	20.879	-0.001	0.152
				0.1523

## DILUTION OF IMMEDIATE PRODUCT OF ZINC REACTION

8	19.588	20.034	-0.003	0.443
9	19.588	20.034	-0.003	0.443
10	19.614	20.058	-0.001	0.443
11	19.609	20.054	-0.002	0.443
12	19.592	20.036	-0.001	0.443
				0.443

The result with hydrochloric acid is essentially identical with that found in a previous research.<sup>9</sup> The calculation of the change in heat-content produced by the respective dilutions leads then to the following quantities.

For pure acid solution  $(15.06 + 125.0 \times 0.849 + 1021.6) 0.1523 = 174.04$  cal.

For acid zinc solution  $(15.06 + 125.0 \times 0.863 + 970.2) 0.443 = 484.2$  cal.

These values must be multiplied by 170/125 and 178.68/125, respectively,<sup>10</sup> to find the heats of dilution of the amounts actually concerned in each experiment involving the solution of zinc in acid; 236.7 and 692.1, respectively, are the results. To correspond with a gram atom of zinc,

<sup>7</sup> Ref. 1, p. 433.

<sup>8</sup> Ref. 2, p. 1178. Ref. 4, pp. 1622, 1625.

<sup>9</sup> Ref. 4, p. 1631.

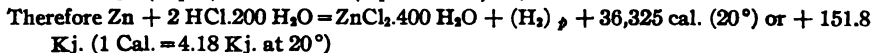
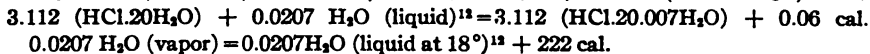
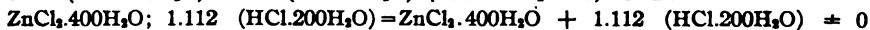
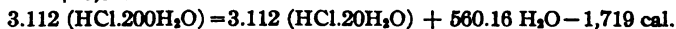
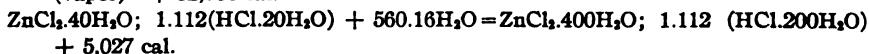
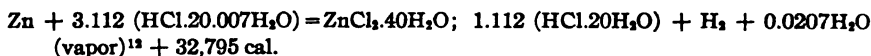
<sup>10</sup> The weight of the product is of course made up of the sum of the weights of acid and zinc less the weight of moist hydrogen evolved  $(170.00 + 9.00 - 0.32 = 178.68)$ . The small amount (0.051) of water lost by evaporation affects the heat of dilution but little.

these values should each be multiplied by 7.2633, yielding 1719 cal. and 5027 cal., respectively. Mixing  $\text{HCl} \cdot 200\text{H}_2\text{O}$  and  $\text{ZnCl}_2 \cdot 400\text{H}_2\text{O}$  was found in two trials to evolve no appreciable amount of heat.

One further calculation is necessary, namely, of the heat of evaporation of the water carried away by the hydrogen. The average vapor pressure of pure water between  $16^\circ$  and  $20^\circ$  is 15.53 mm.; therefore (the average atmospheric pressure during the experiments having been 758 mm.) the average volume of the moist hydrogen in each experiment must have been 
$$\frac{22.4 \times 758 \times 291.1}{742.5 \times 273.1 \times 7.2633} = 3.365 \text{ liters.}$$
 Since at that

average temperature each liter of water vapor weighs 15.29 mg. and the latent heat of evaporation is 593, the evaporation must have needed 30.5 cal. For a gram atom of zinc the quantity of heat absorbed would be 222 cal.<sup>11</sup>

All the data are now at hand for the calculation of the heat of the reaction  $\text{Zn} + 2(\text{HCl} \cdot 200\text{H}_2\text{O})$  at  $20^\circ$ . This calculation may be expressed as follows, the semicolon indicating a mixture of solutions, and all the quantities being expressed on a consistent molal basis:



Instead of this value, 36.32 Cal., Thomsen found 34.2 (in error largely because his correction for dilution was erroneous in principle) and Richards, Rowe and Burgess in their preliminary study found 36.6. The new value is doubtless more accurate than the older ones.

The value 36.32 Cal. corresponds to the isothermal reaction at  $20^\circ$  in which the hydrogen evolved is dry, a condition not attained in practice. To find the actual result of the isothermal reaction at  $20^\circ$  involving moist hydrogen, the latent heat of evaporation of about 0.42 g. of water, that is to say, about 0.25 Cal.,<sup>13</sup> should be subtracted, leaving 36.07 Cal. or 150.8 KJ. as the final result.

<sup>11</sup> For a fuller discussion of this subject see Ref. 1, pp. 450-452.

<sup>12</sup> This quantity of water is too small to affect essentially the heats of dilution. It is important only because of its heat of vaporization, but is introduced in the first and fifth equations for the sake of completeness of thermochemical statement.

<sup>13</sup> The value 0.222 Cal. given previously corresponds to the actual adiabatic reaction between  $16^\circ$  and  $20^\circ$ . The value 0.25 corresponds to the evaporation from the very dilute acid or zinc chloride solution at  $20^\circ$ .

The temperature coefficient of this reaction cannot be computed accurately with the data on hand, since the heat of dilution of the product of the first of these processes has been determined accurately only at a single temperature. Probably, however, it is negative, and may amount to at least 25 cal. per degree, since the product contains one ion less than the factors, and at this concentration is probably less ionized than the factors;<sup>14</sup> de Marignac's experience supports this conclusion.<sup>15</sup> He found that  $\text{ZnCl}_2 \cdot 200\text{H}_2\text{O}$  has 39 less heat capacity than  $2 \text{HCl} \cdot 100\text{H}_2\text{O}$ , and that the difference with double these concentrations was  $-68$ . His specific heat determinations were usually remarkably accurate considering the simple means employed. Our own experience with a still more concentrated acid solution ( $20\text{H}_2\text{O}$ ) which showed a difference of  $-73$  cal. per degree is confirmatory. The difference in heat capacity between metallic zinc and hydrogen is negligible in this connection. Assuming that at infinite dilution the loss of one gram-ion would make a difference of  $+25$ <sup>16</sup> and plotting the smooth, almost linear curve between this value and the values for the two concentrations studied by de Marignac, we arrive at the value of about  $-30$  cal. per degree as the temperature coefficient of the reaction of zinc on  $2 (\text{HCl} \cdot 200\text{H}_2\text{O})$ . Until more direct knowledge is available, this value may be assumed as the most reasonable one.

The value 36.32 Cal. is the heat of reaction corrected for the heat of vaporization of water carried away by the hydrogen, but uncorrected for outside work done against atmospheric pressure by the hydrogen. This

latter amounts to  $\left( \frac{291.1 \times 22.4}{273.1} \right) 0.0242 = 0.58$  Cal. The work done

by the small amount of aqueous vapor (which augmented the volume of hydrogen by about 0.4 liter) has already been accounted for in the heat of its evaporation. Hence the energy change ( $U$ ) of the reaction in question is found to be 36.90 Cal. or 154.2 Kj.

With the help of S. Tamaru, cadmium has been studied in the same way. The result is communicated in the following paper.

We gladly express our obligation to the Carnegie Institution of Washington as well as to an anonymous benefactor of the Laboratory for generous financial support in this investigation.

### Summary

1. A new apparatus is described, suitable for dissolving substances

<sup>14</sup> Richards and Rowe, *THIS JOURNAL*, 43, 793 (1921).

<sup>15</sup> C. de Marignac, "Oeuv. Compl." Geneva. II, 624.

<sup>16</sup> Ref. 14, pp. 793, 795. This is the most probable value for the change of heat capacity caused by the simple subtraction of a single gram-ion. Whether this same change occurs when a bivalent ion takes the place of two univalent ones is not certain, since adequate data are lacking.

in a comparatively small excess of liquid and providing a conveniently large heat capacity for the reception of the heat.

2. With this apparatus the heat of the reaction  $\text{Zn} + 2\text{HCl} \cdot 200\text{H}_2\text{O} = \text{ZnCl}_2 \cdot 400\text{H}_2\text{O} + \text{H}_2$  was found to be 36.32 Cal. (or 151.8 KJ.) if the hydrogen is dry, and 36.07 Cal. (or 150.8 KJ.) if the hydrogen is moist, at 20°.

3. The total energy change ( $U$ ) of this reaction is therefore 36.90 Cal. (or 154.2 KJ.) at 20°.

4. The heats of dilution of factors and products needed for the attainment of these results were found experimentally.

5. Attention was paid to numerous minor details which have usually been overlooked.

6. The temperature coefficient of the heat of solution of zinc in conc. hydrochloric acid is shown to be negative and of considerable magnitude; even with dil. acid it probably amounts to -30 cal. per degree.

CAMBRIDGE 38, MASSACHUSETTS

[CONTRIBUTION FROM THE WOLCOTT GIBBS MEMORIAL LABORATORY, HARVARD UNIVERSITY]

## THE HEAT OF SOLUTION OF CADMIUM IN HYDROCHLORIC ACID

By THEODORE W. RICHARDS AND SETSURO TAMARU

Received March 1, 1922

The importance of a revision of fundamental thermochemical data with modern accuracy has been repeatedly emphasized. Among the metals treated in an earlier preliminary communication, cadmium was the least satisfactorily studied, as was pointed out at the time.<sup>1</sup> Considerable improvement in method, already applied in the case of zinc,<sup>2</sup> was applicable likewise to the case of cadmium, with minor changes. The present paper communicates the result of work carried out during the winter of 1914-1915. The work on zinc having been described in detail, a briefer account now suffices.

In order to gain further experience with the apparatus and to confirm its trustworthiness, a few trials were first made with zinc, repeating the work described in the previous paper just mentioned, under somewhat different conditions. The last two (naturally the most successful) of these experiments each involved the solution of 7.001 g. of zinc in 170.04 g. of  $\text{HCl} \cdot 19.76\text{H}_2\text{O}$  (containing a drop of chloroplatinic acid), surrounded by 943.6 g. of water. The increments of temperature of these two experiments were respectively 3.116° and 3.113°, with all thermometric

<sup>1</sup> Richards and Burgess, *THIS JOURNAL*, 32, 459 (1910). Richards, Rowe and Burgess, *ibid.*, p. 1185.

<sup>2</sup> Richards and Thorvaldson, *ibid.*, 44, 1051 (1922).

corrections applied, the final temperatures being  $20.30^{\circ}$  and  $20.43^{\circ}$  respectively. The total heat capacity was  $1103.4$ ; and  $3.1145^{\circ} \times 1103.4 = 3436.5$ . Corrected for the heat of depositing  $7.5$  mg. of platinum (as will be explained shortly) the result becomes  $3434$  cal., which corresponds to  $0.1071$  gram atom of zinc and  $0.4332$  mol. of  $\text{HCl} \cdot 19.75\text{H}_2\text{O}$ ; hence for  $1.0000$  gram atom of zinc the evolution of heat under these circumstances would be  $32.064$  Cal. This output of heat corresponds to the isothermal reaction at  $20.36^{\circ}$ . According to the previous investigation, it would be  $26$  cal. more at  $20^{\circ}$ , making  $32.090$  Cal. The heat of dilution of the corresponding  $4.045$  mol. of hydrochloric acid is easily found from earlier work;<sup>3</sup> and that of the resulting solution of zinc was duly determined,  $109.34$  g. of this solution (sp. heat =  $0.864$ ) causing a rise of  $0.422^{\circ}$  when diluted with  $869.0$  g. of water in the usual apparatus. The total dilution-effects were thus shown to be respectively  $2.237$  and  $6.238$  Cal. for quantities corresponding to a gram atom of zinc, and the heat removed by evaporation of the water at  $18.8^{\circ}$  with the hydrogen must have been  $234$  cal. Therefore the total output of heat as found in the reaction  $\text{Zn} + 2\text{HCl} \cdot 200\text{H}_2\text{O} = \text{ZnCl}_2 \cdot 400\text{H}_2\text{O} + (\text{H}_2)_g$ , at  $20^{\circ}$  would be  $32.090 + 6.238 - 2.237 + 0.234 = 36.325$  Cal. If Thorvaldson's value for the heat of dilution of hydrochloric acid had been used, the result would have become  $36.335$ . These are in as close agreement as could be expected with the more thorough work of one of us with Thorvaldson, which gave the value  $36.325$ . In the present repetition less zinc was used, involving a change in every one of the corrections.

Such an agreement justified the application of the method to other substances; and no modifications in the apparatus seemed to be necessary. The only important changes were the use of more concentrated hydrochloric acid and the addition of a larger amount of chloroplatinic acid, both changes being necessitated by the lower solution tension of cadmium. The thermometers and their standardization were identical, and precisely the same apparatus of gold and platinum was used in the adiabatic calorimeter, in essentially the same way. The only change in technique was a decrease in the rate of stirring, which was permissible because the reaction with cadmium was somewhat slower and the temperature change was much less. The stirring rate (about  $50$  strokes per minute) caused a rise of only  $0.001^{\circ}$  in  $30$  minutes when the environment was  $0.01^{\circ}$  to  $0.02^{\circ}$  warmer than the calorimeter. Perhaps part of the heat from stirring was balanced by a very small cooling effect from evaporation. In any case, a net correction of  $0.002^{\circ}$  per hour was justified by the performance of the apparatus under the conditions employed.

<sup>3</sup> Richards and Rowe, *THIS JOURNAL*, **42**, 1632 (1920); **43**, 786 (1921). The heat of dilution of  $\text{HCl} \cdot 19.75 \text{H}_2\text{O}$  to  $\text{HCl} \cdot 200\text{H}_2\text{O}$  would be  $553$ , i. e.,  $4$  cal. more than the heat of dilution of  $\text{HCl} \cdot 20 \text{H}_2\text{O}$  to the same limit.



Once more the effect of varying the thickness of the air space, which serves as thermal insulator around the calorimeter, was tested with this apparatus. A thickness of 7 mm. was found to involve a transfer of 0.008 cal. per minute per sq. cm. per  $1^\circ$  thermal head. Enlargement of the space to 18 mm. showed no advantage; restriction to 4.5 mm. raised the amount of heat transferred to 0.0096 cal. This outcome is essentially in agreement with earlier tests of our own and with later work of W. P. White, who has made a very thorough and careful study of this matter.<sup>4</sup>

The adjustment of temperature between the contents of the gold bottle and the surrounding water in the calorimeter was also tested. Naturally, this adjustment was found to be slow when the contents of the bottle were not stirred; but it was completely accomplished within 5 minutes when they were moderately agitated. The evolution of hydrogen provides sufficient stirring at first; at the end of the reaction the final equalization of temperature was accomplished by stirring with the cap beneath the stopper, which was lowered into the liquid of the bottle. Doubtless the hydrogen rising through the liquid develops a trace of heat through friction, but this must be so small as to be negligible.

The specific heats of both the hydrochloric acid and the cadmium solution (after the experiment) were roughly determined, in the apparatus used in the case of thallium amalgams.<sup>5</sup> This apparatus was standardized by pure water. Exactly 40.00 g. of each liquid was taken for each trial and a definite potential was established at the terminals of the heating resistance for varying lengths of time, producing various rises of temperature in the several liquids. The averages of many trials showed that 480.0 seconds with pure water produced a rise of  $4.281^\circ$ , 360.0 seconds with the cadmium solution produced a rise of  $4.167^\circ$ , and 390.0 seconds with the hydrochloric acid ( $\text{HCl} \cdot 10.05\text{H}_2\text{O}$ ) produced a rise of  $4.492^\circ$ . Since the heat capacity of the apparatus was 3.68 cal. per degree, and since the specific heat varies directly as the time and inversely as the temperature increment, the cadmium solution evidently had a specific heat of 0.745 and the hydrochloric acid a specific heat of 0.753. Although these values do not pretend to be very exact, they serve the present purpose. The latter value is consistent with earlier experiments and calculations.<sup>6</sup> The zinc chloride solution mentioned early in this paper was similarly found to have the specific heat 0.864. These specific heats were used in calculating the thermal output of the appropriate reactions.

After a few further preliminary trials with cadmium, four final determinations were made, in each of which (on the average) 169.73 g. of hydrochloric acid (of concentration  $\text{HCl} \cdot 10.05\text{H}_2\text{O}$ , sp. heat 0.753) was used in the gold bottle; 11.024 g. of pure electrolytic cadmium was placed in the stopper and later dissolved in the acid; 0.3 g. of a solution of chloroplatinic acid was added in each case. The flask was surrounded by 799.93 g. of water in the outer platinum vessel. The platinum and gold apparatus and thermometer as before had a total heat capacity of 20.5 and the correction for half the heat capacity of the moist hydrogen

<sup>4</sup> White, *Phys. Rev.*, 7, 682 (1916).

<sup>5</sup> Richards and Daniels, *THIS JOURNAL*, 41, 1732 (1919).

<sup>6</sup> Ref. 3, p. 1631.

evolved was 0.4, so that the heat capacity of the system was 948.7. There were small deviations from these values in individual cases, but in no case was the deviation enough to produce a significant effect upon the results. Even considerable variations would not have vitiated the exact use of the averages in connection with *average* values in the tables below. The last column of the table gives the products of the values in the preceding column multiplied by 948.7.

TABLE I  
SOLUTION OF 11.024 G. OF CADMIUM IN 189.73 G. OF HCl.10.05H<sub>2</sub>O

Expt.	$t_1$ °C.	$t_2$ °C.	$t_2 - t_1$ °C.	Stirring correction °C.	$\Delta t$ corrected °C.	Heat evolved Cal. (19°)
1	17.929	19.896	1.967	-0.002	1.965	1,864
2	18.062	20.033	1.971	-0.001	1.970	1,869
3	17.744	19.708	1.964	-0.002	1.962	1,861
4	17.450	19.420	1.970	-0.002	1.968	1,867
Av.		19.77			1.9662	1,865

On the average 48 mg. of platinum was deposited in each experiment, (0.039 in the form of powder as well as 0.009 upon the gold vessels, as determined by the increase in their weight). From the value 1,865 cal. must therefore be subtracted 18 cal., since it has been shown<sup>7</sup> that every gram atom of platinum precipitated evolves in the process 73 Cal. more heat than the evolution of the equivalent amount of hydrogen. This leaves 1,847 cal., corresponding to the given amount of metal, or 18,832 cal. corresponding to 112.40 g. (the gram atom) of cadmium. In 20° Calories this value becomes 18.838. This value, 18.838 Cal., is the heat of the main reaction concerned: the solution of cadmium at 19.77° in a fairly concentrated acid, present in considerable excess (7.956 mol per gram atom of metal). The result is uncorrected for loss of heat from evaporation of water and for the work done (against the atmosphere) by the moist hydrogen. At 20° it would be 18.822 Cal. (as explained later) since the change of heat capacity is 71 cal./t°.

To find the heat of reaction of cadmium on an exactly equivalent amount of hydrochloric acid in dilute solution, this value just given must, of course, be corrected for the heats of dilution of factors and products. The heat of dilution of HCl.10.00H<sub>2</sub>O to 200H<sub>2</sub>O is known, being 1161 cal. per mol.<sup>8</sup> The curve showing heats of dilution at various concentrations shows that this quantity with moderate concentrations is nearly a simple linear function of the concentration,<sup>8</sup> hence the heat of the reaction  $\text{HCl.10.05H}_2\text{O} + 189.95\text{H}_2\text{O} = \text{HCl.200H}_2\text{O}$  is 1155 cal. Since 7.956 mols of hydrogen chloride was used per gram atom of cadmium, the

<sup>7</sup> Richards and Burgess, Ref. 1, p. 454.

<sup>8</sup> Richards, Rowe and Burgess, Ref. 1, p. 1178.

heat of dilution to be subtracted on this account is  $7.956 \times 1.155 = 9.189$  Cal.

With the same apparatus as that used to obtain this datum, we determined the heat of dilution of the product of the reaction, diluting 63.96 g. of the acid cadmium chloride solution to the equivalent extent with 943.6 g. of water, in five successive independent trials. The five experiments had final temperatures averaging  $19.75^\circ$ , and yielded the values  $0.253^\circ$ ,  $0.255^\circ$ ,  $0.253^\circ$ ,  $0.252^\circ$ , and  $0.254^\circ$ , averaging  $0.2534^\circ$ , for the temperature increment on dilution. The heat capacity of the cadmium solution was 47.5 (since its specific heat had been found to be 0.745) and the apparatus had a capacity of 15.1. Hence the total heat capacity warmed in these dilutions was 1,006.3 cal. per degree; therefore the heat evolved was 0.2550 Cal. Multiplying this result by  $2.821 \times 10.196$  to reduce to the equivalent of a gram atom of cadmium, the heat value for the dilution of the total resulting solution containing exactly a gram atom of cadmium is found to be 7.336 Cal. (at  $19.75^\circ$ ). Corrected to  $20^\circ$  this becomes 7.365 Cal.<sup>9</sup> Hence the heat of reaction of cadmium on the exactly equivalent amount of  $\text{HCl} \cdot 200\text{H}_2\text{O}$ , evolving moist hydrogen under constant pressure, would be  $18.822 - 9.189 + 7.365 = 17.00$  Cal. The average heat of evaporation of the water carried away by the hydrogen between the temperature  $17.8^\circ$  and  $19.75^\circ$  would be for a gram molecule of hydrogen 234 cal. Adding this quantity the final expression is obtained.



This result, 17.23, (72.0 kJ.) is almost identical with that (17.2) found in the preliminary work. The close agreement is partly accidental, since the earlier result had a large possible error. Even the present value 17.23 has a greater range of possible experimental error than the result with zinc, since cadmium requires moderately concentrated hydrochloric acid for solution, and the heats of dilution of factors and products are therefore necessarily rather large. In the present case an error of  $0.001^\circ$  would cause an error of 0.05% in the main reaction, of 0.3% in the heat of dilution of hydrochloric acid and of 0.4% in the heat of dilution of the product of the reaction. If all these errors should happen to tend in the same direction (which is, of course, unlikely) the error of the final result would be 0.07 Cal. Thus when the heat evolved on dilution is large, as in the present case, these temperature changes should be measured much more accurately than that of the main reaction. It is hoped that the recent gains in accuracy in thermometric measurement may make possible in the near future a closer evaluation of these quantities, leading perhaps to slight revision of the value just given. For the present, however,

<sup>9</sup> On the fairly safe assumption that the change of heat capacity of this solution is nearly the same as that of hydrochloric acid of that concentration. (See Ref. 3).

this value seems to be more trustworthy than any other which has been published and therefore, even though somewhat tentative, is worthy of record. Calculated to correspond strictly with the isothermal reaction at 20° (the hydrogen being evolved moist from the very dilute acid solution), the value becomes 16.98.

Thomsen's value, 17.6, was distinctly too large, whereas his value for zinc was distinctly too small. This difference in sign of the error is dependent upon the fact that although the dilution of zinc chloride gives out much more heat than the dilution of the equivalent concentration of hydrochloric acid, on the other hand, the dilution of cadmium chloride gives out less heat than the dilution of the equivalent amount of hydrochloric acid. The heats of dilution of the metallic chloride solutions were entirely overlooked by Thomsen.

The temperature coefficient of this heat of reaction cannot be exactly computed with the data at hand. However, since the heat capacity of the contents of the gold flask (together with the hydrogen) increased about 7. cal. per degree during the main reaction, the temperature coefficient of the heat of reaction of a gram atom of cadmium upon excess of hydrochloric acid (4 times the stoichiometric amount of  $\text{HCl} \cdot 10\text{H}_2\text{O}$ ) in this way must be about  $-71$  cal. per degree. This is not far from the temperature coefficient of the heat of the corresponding zinc reaction,  $-74$  cal. per degree, although the conditions were not exactly the same, the acid having been less concentrated and in smaller excess in the case of the zinc. Probably even in dilute solutions there is a gain of heat capacity in dissolving cadmium in hydrochloric acid, as in the case of zinc; and theoretical conclusions point to a similar temperature coefficient of the heat of the dilute reaction amounting, perhaps to about  $-30$  cal. per degree.

The correction for the work done by the hydrogen evolved is, of course, identical with that in the case of zinc at the same temperature. Therefore the total energy change ( $U$ ) = 17.81 Cal. or 74.4 kJ. at 20°.

The earlier work (of Burgess and one of us) on magnesium needs no revision of this kind, since the acid was diluted in the first place; but the cases of iron and aluminum await further study.

We are indebted once more to the Carnegie Institution of Washington, as well as to an anonymous benefactor of this Laboratory, for generous financial support in this investigation.

### Summary

1. With the apparatus recently described in the case of zinc, the heat of reaction  $\text{Cd} + 2\text{HCl} \cdot 200\text{H}_2\text{O} = \text{CdCl}_2 \cdot 400\text{H}_2\text{O} + (\text{H}_2)_p$  is found to be 17.23 Cal. (or 72.0 kJ.) at 20° if the hydrogen is dry; and 16.98 Cal. (or 71.0 kJ.) if the hydrogen is moist, (at 20.0° and 760 mm.).

2. The total energy change,  $U$ , of the reaction is therefore 17.81 Cal. (or 74.4 kJ.) at 20°.

3. The specific heats of factors and products and the heat of dilution of the product needful for the attainment of these results were found experimentally.

4. The temperature coefficient of the heat of solution of cadmium in conc. hydrochloric acid is shown to be negative,  $-71$  cal. per degree; probably even with dilute acid it amounts to as much as  $-30$  cal. per degree.

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[CONTRIBUTION FROM THE GATES CHEMICAL LABORATORY OF THE CALIFORNIA INSTITUTE OF TECHNOLOGY, No. 13]

## THE CRYSTAL STRUCTURE OF AMMONIUM FLUOSILICATE

By RICHARD M. BOZORTH<sup>1</sup>

, Received March 22, 1922

### 1. Introduction

Ammonium fluosilicate,  $(\text{NH}_4)_2\text{SiF}_6$ , exists in two crystalline forms,<sup>2</sup> cubic and hexagonal. The cubic form is the stable one at ordinary temperatures, while the hexagonal form has been obtained<sup>3</sup> below  $5^\circ$ . It seemed probable that the cubic form has the same structure as ammonium chloroplatinate studied by Wyckoff and Posnjak,<sup>4</sup> and ammonium and potassium chlorostannate studied by Dickinson;<sup>5</sup> but complete evidence of iso-morphism was lacking.<sup>6</sup> It was therefore desirable to study its crystal structure, not only to determine whether it is the same as that of these other salts, but also to measure the size of the unit of structure and the distances between the centers of the various atoms.

Crystals of the fluosilicate were prepared by the spontaneous evaporation at room temperature of an aqueous solution containing an excess of hydrofluoric acid.

The methods employed for obtaining the X-ray data and for the interpretation of these data are essentially those used by Wyckoff and Posnjak and by Dickinson, to whose articles reference may be made for more detailed information.

I wish to express my thanks to Dr. R. G. Dickinson for valuable advice during the progress of this research.

### 2. Determination of the Size of the Unit-cube and the Number of Molecules in It

Photographs of line spectra from the (111) face of a crystal showed

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<sup>2</sup> Groth, "Chemische Krystallographie," Engelmann, Leipzig, 1906, vol. 1, p. 485.

<sup>3</sup> Gossner, *Z. Kryst. Mineral.*, **38**, 147 (1904).

<sup>4</sup> Wyckoff and Posnjak, *THIS JOURNAL*, **43**, 2292 (1921).

<sup>5</sup> Dickinson, *ibid.*, **44**, 276 (1922).

<sup>6</sup> Ref. 2, p. 466.

five orders of reflection. From the values of the angles of the reflections and the density of the salt, determined to be 2.01, the smallest possible number of molecules in the unit of structure was found in the usual way to be 4, as in the other salts mentioned above.

Table I gives the angles of reflection, the orders of the reflections, and the length in Ångstrom units of the unit-cube based on this conclusion. In calculating the number of molecules in the unit and the length of the unit-cube the wave length<sup>7</sup> of the rhodium  $\alpha_1$  line was taken to be 0.6121 Ångstrom units.

TABLE I

THE X-RAY REFLECTIONS OF THE RHODIUM  $\alpha_1$  LINE FROM THE (111) FACE

Angle of reflection	Order of reflection	Length of unit-cube	Intensity of reflection
3° 38'	1	8.37	strong
7° 15'	2	8.40	strong
10° 56'	3	8.38	medium weak
14° 39'	4	8.38	medium weak
18° 26'	5	8.38	weak
From the density		8.37	
Final value		8.38	

### 3. The Laue Photographic Data

Laue photographs were then taken with a beam of X-rays passing through the (111) face, and these photographs analyzed by the usual methods.

The data which were useful in determining the positions of the fluorine atoms are given in Table II. The interplanar distances and wave lengths are expressed in Ångstroms. The smallest wave length calculated for any spot on a Laue photograph was 0.27 Ångstrom units. Wave lengths lower than 0.26 were considered to be absent from the spectrum.

TABLE II

DATA FROM THE LAUE PHOTOGRAPHS

Photograph No. 1. Photograph No. 2. Photograph No. 3

Reflecting plane	Inter-planar distance	Wave length of reflected X-rays		Wave length of reflected X-rays		Wave length of reflected X-rays		Calculated amplitude for $\mu = 0.205$
		Intensity of spot produced	Intensity of spot produced	Intensity of spot produced	Intensity of spot produced	Intensity of spot produced		
First-Order Reflections								
(135)	1.42	0.40	0.9	0.47	3	..	..	1.2
(531)	1.42	0.49	1.0	..	..	..	..	1.2
(335)	1.28	0.48	0.3	0.50	0.4	..	..	0.2
(353)	1.28	..	..	..	..	0.46	0.5	0.2
(155)	1.17	0.52	1.5	0.49	4	..	..	2.8
(117)	1.17	..	..	..	..	0.46	0.6	0.4
(535)	1.09	..	..	0.46	2.5	..	..	1.8
(731)	1.09	0.31	0.0	0.42	0.05	..	..	0.5
(373)	1.02	0.47	0.4	0.37	0.4	..	..	1.5

<sup>7</sup> Duane, *Bull. Nat. Research Council*, 1, No. 6 (1920).

TABLE II (continued)  
 Photograph No. 1. Photograph No. 2. Photograph No. 3

Reflecting plane	Inter-planar distance	Wave length of reflected X-rays	Intensity of spot produced	Wave length of reflected X-rays	Intensity of spot produced	Wave length of reflected X-rays	Intensity of spot produced	Calculated amplitude for $\mu = 0.205$
First-Order Reflections								
(557)	0.84	0.46	0.4	0.47	0.6	..	..	1.7
(359)	0.78	0.36	0.2	0.40	0.3	..	..	0.9
(593)	0.78	0.32	0.1	..	..	0.46	0.5	0.9
(775)	0.76	0.50	0.0	0.44	0.0	..	..	0.0
(1-1-11)	0.76	..	..	..	..	0.46	0.4	1.2
(559)	0.73	0.45	0.3	0.49	0.5	..	..	3.0
(197)	0.73	0.44	0.1	0.41	0.1	..	..	0.7
(11-1-3)	0.73	0.46	0.05	0.52	0.1	..	..	0.2
(11-1-5)	0.69	0.46	0.2	0.47	0.2	..	..	1.8
(759)	0.67	0.46	0.1	0.41	0.1	..	..	1.3
(5-5-11)	0.64	0.44	0.2	0.47	0.3	..	..	2.4
Second-Order Reflections								
(121)	3.42	..	..	0.40	0.4	..	..	0.3
(212)	2.79	..	..	0.48	0.2	..	..	0.0
(123)	2.24	0.35	0.4	0.41	0.9	..	..	1.1
(043)	1.68	0.45	0.1	0.41	0.1	..	..	0.5
(324)	1.56	0.52	0.0	0.47	0.0	..	..	0.1
(350)	1.44	0.48	0.5	0.41	0.5	..	..	3.2

#### 4. Interpretation of the Data

The possible arrangements for ammonium fluosilicate permitted by the theory of space groups are those considered for ammonium chloroplatinate by Wyckoff and Posnjak, and for ammonium chlorostannate by Dickinson. The correct arrangement in this case is the same one that they have found, and can be proved in the same way. The intensity functions are accordingly of the same form.

For purposes of comparing intensities, planes may be divided into three classes, namely: (1) planes all of whose indices are odd; (2) planes having two odd indices and one even; (3) planes having one odd index and two even. Planes of Classes 2 and 3 reflect only in even orders.

The value of the parameter  $\mu$ , which fixes the position of the fluorine

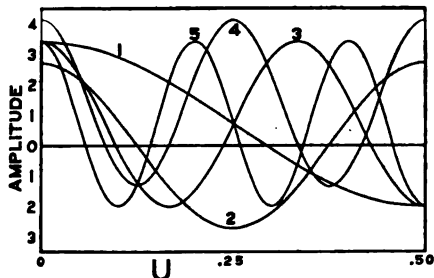


Fig. 1.

atoms, was first limited to the region between 0.19 and 0.25 by the following method. It was observed on the spectral photographs that the fourth-order reflections from the (111) face were as strong as the third-order reflections. It was therefore concluded that the fourth-order amplitude must be greater than the third-order ampli-

tude. The amplitudes calculated for all five orders from the (111) face are plotted for all distinct values of  $u$  in Fig. 1. The regions which show a greater fourth-order than third-order amplitude can be noted. It was concluded

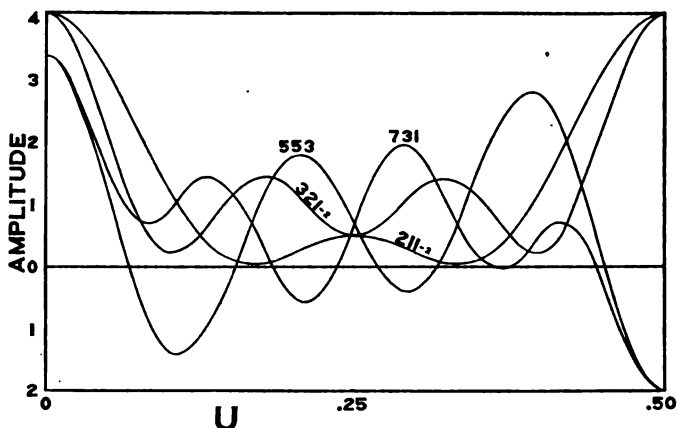


Fig. 2.

from Laue photographic data that (553) must have a larger amplitude than (731) in the first order, and (321) a larger amplitude than (211) in the second order. The calculated amplitudes of these forms are plotted for all distinct values of  $u$  in Fig. 2. It will be seen from Figs. 1 and 2 that the only values of  $u$  which account for these data are those between 0.19 and 0.25. To limit further the value of  $u$  a plot was made showing the amplitudes of planes of Class 1 for values of  $u$  between 0.19 and 0.25. The original plot included all planes having an interplanar distance of more than 0.64 Ångström units, which is the interplanar distance for (11·5·5), the most complex plane observed. In Fig. 3 are reproduced only those curves which were most useful. Certain inequalities in amplitude were established from the Laue photographic data, and the value of  $u$  more definitely determined with the aid of the figure. For example, since  $(11·5·1) > (971)$ ,  $u < 0.218$ ;

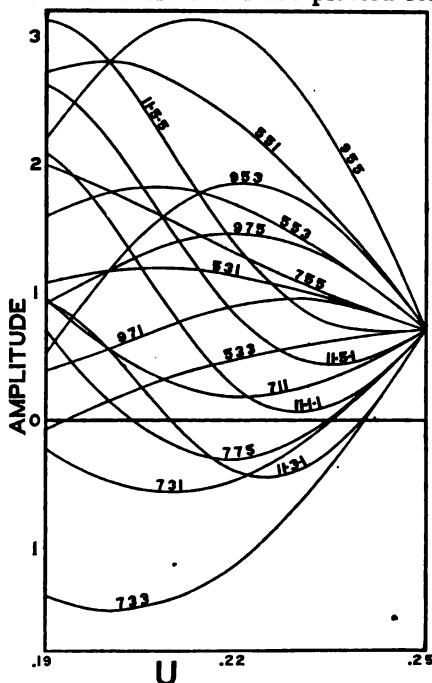


Fig. 3.



since  $(11.5.1) > (975)$ ,  $u < 0.211$ ; since  $(711) < (533)$ ,  $u < 0.218$ ; since  $(955) > (11.5.1)$ ,  $u > 0.195$ ; and since  $(971) \geq (11.3.1)$ ,  $u > 0.200$ . The value of  $u$ , therefore, lies between 0.200 and 0.208. The best value is considered to be 0.205.

In calculating the amplitudes given in the last column of Table II it has been assumed that the reflecting power of each atom is proportional to its atomic number; but the determination of  $u$  based on the comparisons that have been made is largely independent of this assumption, since any reasonable values of the reflecting powers would lead to the same conclusion. However, comparisons between planes of different classes, or even between planes of the same class where at least one of the amplitudes is small or opposite in sign to the other, can be made properly only with a good knowledge of reflecting powers. In view of these limitations all the comparisons which have been properly made are satisfied remarkably well when  $u = 0.205$ . Many of these comparisons may be made with the data of Table II, using the calculated amplitudes given in the last column.

## 5. Conclusions as to the Structure

### Summary

The crystal structure of ammonium fluosilicate has been shown to be like that of ammonium chloroplatinate, ammonium and potassium chlorostannates, namely the structure is that<sup>8</sup> of calcium fluoride,  $\text{CaF}_2$ , in which each fluorine atom is replaced by an ammonium group, and each calcium atom by a fluosilicate group with the 6 fluorine atoms equidistant from the silicon atom in the directions of the axes of the crystal. The length of the cube constituting the unit of structure containing 4 molecules was found to be 8.38 Ångstrom units; the corresponding lengths for the three other complex salts just mentioned are 9.84 for ammonium chloroplatinate, 10.05 for ammonium chlorostannate, and 9.96 for potassium chlorostannate. The shortest distance between the centers of the atoms of fluorine and silicon is 1.72 Ångstrom units, while the sum of the Bragg radii<sup>9</sup> for these atoms is 1.84. The corresponding distances between the platinum or tin and the chlorine atoms in the other three salts are 2.3 Ångstrom units for ammonium chloroplatinate, 2.46 for ammonium chlorostannate and 2.44 for potassium chlorostannate.

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<sup>8</sup> See W. H. and W. L. Bragg, "X-Rays and Crystal Structure," G. Bell and Sons, Ltd., London, 1916, p. 107.

<sup>9</sup> W. L. Bragg, *Phil. Mag.*, **40**, 180 (1920).

## NOTES

**A Cell for the Observation of Colloidal Solutions for Use with Substage Ultra-condensers.**—In laboratories where an ultramicroscope of the Siedentopf and Zsigmondy type is not available, one of the various types of substage dark field condensers, such as the paraboloid or cardioid, is usually employed for the examination of colloids.

It has been stated that such a means of ultramicroscopic observation is useless for direct quantitative work.<sup>1</sup>

Burton<sup>2</sup> has, however, shown how a hemacytometer slide may be used for the estimation of the number of particles in a colloidal solution.

The method has the inconvenience that it is necessary to remove the slide and to readjust the optical arrangement in order to examine a fresh sample of solution. Extended counts become, therefore, somewhat tedious.

An apparatus has been constructed by means of which a series of solutions or of samples of the same solution may be passed through the cell without disturbing the adjustment.

The apparatus which is shown in plan and section in the figure consists principally of a brass block A which is bored at points diametrically opposite to receive two copper tubes of about 2 mm. internal diameter. The tubes fit closely into the holes and are further held by externally soldering. To the bottom of the brass block, which is ground perfectly flat, is cemented a carefully selected cover glass B. The writer used Canada balsam, though this is not an ideal cement to unite metal to glass. Whatever cement is used, the glass must approach closely and uniformly to the brass to ensure that the lower surface of the glass is perfectly flat.

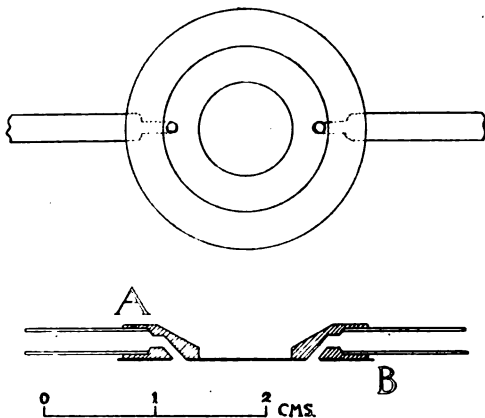


Fig. 1.

When the cover glass is cemented in position, two holes are bored through it to meet the holes in the brass block. This is a very easy operation if a piece of wood through which are bored two holes of the desired diameter and position is temporarily cemented to the glass with some water-soluble cement such as ordinary glue. The holes are bored by means of a copper tube charged at the end with carborundum and glycerine, the tube ro-

<sup>1</sup> King, "Third Rep. Brit. Assoc. Colloid Chemistry," p. 36.

<sup>2</sup> Burton, "Physical Properties of Colloidal Solutions," 1921, p. 124.

tating in the wooden block which can afterwards be removed by soaking in water.

It will thus be seen that the arrangement has the advantage of a reinforced cover glass and as both surfaces of cover glass and slide are flat it will be found unnecessary to cement the two together. The apparatus is held in position on the slide, while being fixed in the microscope by two lumps of plasticine, one on each copper tube, and is further held in position by the spring clips of the microscope stage which press on the tubes.

To the copper tubes are affixed a delivery funnel with a clip and an exit tube.

By opening the clip it will be found that the colloid solution passes through the cell. Since the hemacytometer slides contain a channel round the central portion, it was at first feared that the solution might go round this channel instead of over the graduated portion. By observing the motion through the microscope, it can be seen that this is not the case.

Moreover, it can be very easily seen when the liquid is running through the cell whether any particles are stuck to the bottom of the cell or on the cover glass. This is an important advantage, as such particles, which may be of foreign matter, may constitute a serious source of error in counting the number of particles in a solution.

It would be an additional advantage to gold-plate the whole of the metal portion.

Finally it may be stated that it is easy to obtain such hemacytometer slides of any specified thickness to suit the particular ultra-condenser, and of any desired depth of cell. The writer has used slides of thickness 1.1 to 1.2 mm. to suit a Zeiss Paraboloid, and of depth 0.1 mm. and 0.02 mm. made by Messrs. Hawksley of London.

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Received Feb. 27, 1922

**Instability of Phthalate Potentials.**—The note by Oakes and Salisbury on the instability of phthalate potentials, an instability which seems to have been observed by Merrill, is completely at variance with the author's experience. In the course of several years' work with the hydrogen electrode, 0.05 *M* potassium hydrogen phthalate solutions have been used as a "working standard" and have given no evidence of instability which could be considered convincing. It goes without saying that among hundreds of measurements there have occurred occasional potentials which could justly be called abnormal. Once on leaving an electrode, having an exceptionally light coating of iridium, in contact with a phthalate so-

lution, the potential drifted in a direction opposite to that noted by Oakes and Salisbury and entirely out of the range of any possible hydrogen-ion concentration. Indicator measurements showed that no significant change in Sørensen value had taken place in the solution. However, the electrode had turned bright. Occasionally, "abnormal" potentials, suggesting a change of about 0.05 Sørensen units, have been noted.

Since the method used in almost every case permits the rapid attainment of equilibrium, it might be assumed that the period of the experiment was in no case sufficient to have detected drifts. However, Oakes and Salisbury record a rate of drift which would at once have been detected in the author's apparatus.

With the suspicion that previous observations might have been clouded by a slow and undetected drift where Oakes and Salisbury encountered a rapid one, I have recently set up an outfit not designed for accurate control of liquid-junction potential differences but better adapted for observations over long periods than the shaking electrode vessel. Duplicate vessels were used, holding in one case an electrode of iridium gray on gold-plated platinum and in the other case two electrodes, one of platinum black on gold-plated platinum and the second of palladium black on rhotanium alloy. The drifts over 24 hours were within one millivolt. For the last 18 hours no drift amounting to more than 0.000,05 volt (the limit of the potentiometer's adjustment) was detected. No change in the Sørensen value of the solution was detected with indicators.

I am at a loss to account for the radical difference in my observations and those of Oakes and Salisbury, and must say that after several years' use by others phthalate has not to my knowledge fallen under suspicion in the manner noted by Oakes and Salisbury.

WASHINGTON, D. C.

WM. MANSFIELD CLARK

Received Feb. 18, 1922

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[CONTRIBUTION FROM THE LABORATORIES OF THE ROCKEFELLER INSTITUTE FOR MEDICAL RESEARCH]

## SYNTHESES IN THE CINCHONA SERIES. VII. 5,8-DIAMINO-DIHYDROQUININE AND 5,8-DIAMINO-6-METHOXYQUINOLINE AND THEIR CONVERSION INTO THE CORRESPONDING AMINOHYDROXY AND DIHYDROXY BASES<sup>1</sup>

BY WALTER A. JACOBS AND MICHAEL HEIDELBERGER

Received July 22, 1921

In a former communication<sup>2</sup> amino-azo dyes prepared from 5-amino-dihydroquinine and the analogous 5-amino-6-methoxyquinoline were described. These substances were shown to be easily converted by acids into the corresponding hydroxyazo dyes. By reduction of 8-(*p*-sulfo-

<sup>1</sup> Presented at the Annual Meeting of the American Chemical Society, New York, September, 1921.

<sup>2</sup> THIS JOURNAL, 42, 2278 (1920).

phenylazo)-dihydroquinine we have now prepared 5,8-diamino-dihydroquinine. The base itself is a yellow amorphous powder which crystallizes with great difficulty and rapidly undergoes alteration on exposure to light and air. Like 5-amino-quinoline, it dissolves in dilute acids to form red solutions and yields crystalline salts of which the vermilion tetrahydrobromide and the brown basic sulfate have been studied.

As in the parent amino-azo dyes, it was not surprising to find the amino group here also easily replaceable by hydroxyl. In fact, this occurs so readily that it was at first found difficult to select conditions for the isolation of the polyacid salts. Lability, however, was not confined to the amino group in Position 5, but was shown also by that in Position 8, for on long standing in the cold or on boiling with 1:1 hydrochloric acid 5,8-dihydroxy-dihydroquinine was formed. This substance was isolated as the beautifully crystalline red dihydrochloride which forms orange-red solutions. The instability of the free base prevented its isolation in crystalline form.

From numerous tests that were made, the impression was gained that the amino group in Position 5 was the more readily replaced and that 8-amino-5-hydroxy-dihydroquinine was formed as an intermediate product. Unfortunately, the isolation of this substance from the reaction mixture was rendered very difficult by its properties. We have, however, obtained indirect evidence of its formation by a parallel study of the effect of acids on diamino-methoxyquinoline as described below. 5-Hydroxy-8-amino-dihydroquinine was, however, obtained directly as a tin double salt by reduction of 5-hydroxy-8-phenylazo-dihydroquinine;<sup>3</sup> but the instability of the free aminophenol and the solubility of its simple salts prevented their isolation and study. Like the preceding compounds, solutions of the latter are orange-red.

By boiling diamino-dihydroquinine with conc. hydrobromic acid, which should demethylate as well as desaminate it, yellow needles of an easily soluble hydrobromide of what is probably the 5,6,8-trihydroxy dihydrobromide were obtained mixed with ammonium bromide, but other work intervened to prevent its further study. We hope to complete this study at a later date, as well as the alkylation of the di- and trihydroxy-dihydroquinines.

Parallel with the above studies, 5,8-diamino-6-methoxyquinoline was prepared from the corresponding sulfo-phenylazo dye. The latter was also converted into the 5-hydroxy-8-phenylazo dye, from which 8-amino-5-hydroxy-6-methoxyquinoline was obtained on reduction. On warming diamino-methoxyquinoline with 10% hydrochloric acid, it was possible to isolate as the main product of the reaction an amino hydroxy compound identical with that of known composition obtained from the above hy-

<sup>3</sup> Ref. 2, p. 2280.

droxyazo dye. From this it is evident that the amino group in Position 5 is more labile than that in Position 8.

Finally, by boiling the diamino compound with stronger hydrochloric acid both amino groups were replaced, with the production of 5,8-dihydroxy-6-methoxyquinoline.

The quinoline compounds proved to be more stable than the dihydroquinine derivatives and were readily obtained in crystalline form.

It was also of interest to determine whether the methoxy group in Position 6 contributed to the lability of these amino groups, since it had been already ascertained in our previous work with the amino-azo dyes that those obtained from 5-aminoquinoline itself were much more resistant to the action of acids than the 6-methoxy compounds. 5,8-Diaminoquinoline proved to be even more resistant than its parent azo dye, since boiling it for many hours with hydrochloric acid resulted in the cleavage of but a trace of ammonia. The substitution of Position 6 in these compounds is therefore a determining factor as regards the replaceability of the amino group by hydroxyl by the action of boiling acids.

### A. Derivatives of Dihydroquinine

**5,8-Diamino-dihydroquinine.**—Sixteen g. of 5-amino-8-(*p*-sulfo-phenylazo)-di-hydroquinine<sup>4</sup> were dissolved in 80 cc. of 50% acetic acid and treated with 16 g. of stannous chloride in 50 cc. of 1:1 hydrochloric acid. A gelatinous mass of the tin compound of the unreduced dye was first formed, and this was rapidly dissolved as it was stirred and the reduction proceeded. The mixture warmed considerably and changed to a deep brownish-red solution from which the yellow tin double salt of the diamino compound commenced to separate. The mixture was diluted with water and poured into ice and an excess of alkali, the diamino-dihydroquinine precipitating as yellow flocks. The collected precipitate was washed thoroughly with water, during which the exposed portion darkened perceptibly. Dried in a desiccator it formed a tan colored friable mass. The crude product was dissolved in a small volume of benzene, and the deep brown-olive solution cleared with bone black and filtered as quickly as possible. The deeply colored filtrate was treated with ligroin in amount sufficient to precipitate the product as a brown paste which rapidly hardened to a brittle mass. This was filtered quickly, washed with ligroin and dried in a desiccator containing paraffin, during which it lightened in color to a brown-yellow shade. The yield was 8 g. On exposure to light and air the base gradually darkened. All attempts to crystallize the amorphous substance have proved futile, except in one case in which we observed that during the collection of the base from the benzene and ligroin mixture, the mother liquor slowly deposited more of the substance which appeared under the microscope as minute yellow needles. These possessed all the properties of the former product with the exception of the melting point but, unfortunately, the amount was too small for analysis and its use as seeding material in attempts to crystallize the amorphous base was without result.

The amorphous base darkens above 90°, gradually shrinks together and melts from 125° to 140° with decomposition. The crystalline material, however, melted at 85 to 90° to a dark tar. The amorphous base is easily soluble in the usual organic solvents except ligroin, forming dark brownish-red solutions. In dilute acids it forms deep brown-red solutions which, on standing or more rapidly on heating, no longer give a

<sup>4</sup> Ref. 2, p. 2281.

precipitate of the base when treated with an excess of alkali, but yield solutions which smell strongly of ammonia.

*Analyses.* Calc. for  $C_{30}H_{28}O_2N_4$ : C, 67.40; H, 7.86; N, 15.71. Found: C, 68.00; H, 7.82; N, 15.59.

**THE TETRAHYDROBROMIDE.**—The amino-azo dye was also readily reduced to the diamino base as follows. Five and a half g. of the dye were dissolved in a mixture of 55 cc. of alcohol and 55 cc. of conc. ammonia, and the deep red solution was saturated with hydrogen sulfide. The color changed to a deep yellow-brown and, as the base did not separate, the mixture was poured into a separatory funnel, shaken with ether, and then without removing the ether an excess of ammonia was added and the mixture again shaken. This procedure removed free hydrogen sulfide and avoided the formation of pasty lumps of the base which are difficult to disintegrate and dissolve. After drying the ether extract and concentrating, the base was left as a dark syrup. On dissolving this in a small volume of cold water and sufficient cold hydrobromic acid to make the solution acid to congo red, the addition of sodium bromide accompanied by rubbing caused 5 g. of lustrous golden scales to separate. These were filtered off and washed with acetone, the color changing to an orange-red. A solution of the salt in 12 cc. of warm water was cooled and treated with sufficient strong hydrobromic acid to cause crystallization. The salt separated slowly as vermilion needles and prisms which were air-dried. It is easily soluble in water and in alcohol, forming deep red solutions. The analytical results were not all that could be desired, but with a substance so sensitive to the action of acids and so easily hydrolyzed we were unable to improve upon them.

*Analyses.* Calc. for  $C_{30}H_{28}O_2N_4 \cdot 4HBr$ : N, 8.24; Br, 47.04. Found, air-dry: N, 8.00; Br, 49.29. Salt dried in desiccator over  $H_2SO_4$ : N, 8.47; Br, 41.80.

**THE SULFATE.**—The brown-red ether extract of the base obtained by the reduction of 16 g. of dye by either method was washed with water and then shaken out with 50 cc. of *N* acetic acid. The deep brown-red aqueous layer was filtered rapidly and treated with saturated ammonium sulfate solution. On rubbing, the sulfate crystallized as a yellow-brown powder consisting of microscopic 6-sided polyhedra, while the mother liquor retained dark impurities. The yield was excellent. The salt was washed with ice water and recrystallized in small portions by dissolving it in hot water and adding a little ammonium sulfate solution to the dark yellow-brown solution. When cooled and rubbed the solution deposited the salt as a brown powder consisting of globules or hexagonal crystals which darken rapidly and undergo decomposition. The anhydrous substance darkens above  $160^\circ$  and melts and decomposes at  $220-225^\circ$ .

Although the salt is obtained from an acid solution, it is rather surprising that, judged by analytical data, the substance is a basic sulfate.

In the analysis of the substance, water was determined by drying it over sulfuric acid at room temperature, and sulfur by the Carius method.

*Analyses.* Calc. for  $(C_{30}H_{28}O_2N_4)_2 \cdot H_2SO_4 \cdot 5H_2O$ :  $H_2O$ , 10.00. Found:  $H_2O$ , 10.68. Calc. for  $(C_{30}H_{28}O_2N_4)_2 \cdot H_2SO_4$ : C, 59.22; H, 7.16; N, 13.82; S, 3.96. Found: C, 58.50; H, 7.21; N, 13.87; S, 4.35.

**5-Hydroxy-8-amino-dihydroquinine (tin double salt).**—Fourteen and a half g. of 5-hydroxy-8-phenylazo-dihydroquinine<sup>3</sup> were dissolved in 100 cc. of alcohol by the addition of a few cubic centimeters of acetic acid, warmed, shaken vigorously and treated as quickly as possible with a warm solution of 18 g. of stannous chloride in 100 cc. of 10% hydrochloric acid. The thick paste which first formed dissolved rapidly as the reduction proceeded, giving a deep red solution from which a good yield of the tin double salt of the aminophenol quickly separated as lustrous golden-yellow needles and leaflets. These were filtered, washed with 10% hydrochloric acid, and recrystallized from 50% acetic acid, from which the salt separated in the same form. The substance was dried in a

desiccator over sulfuric acid and sodium hydroxide. The salt darkens above 200°, but does not melt when heated to 280°. It is fairly soluble in water or dilute alcohol, especially on warming, yielding orange-red solutions. It is practically insoluble in alcohol or acetone. It dissolves in alkali, forming a clear, light brown solution which deposits light colored flocks on standing. Ferric chloride, added to the aqueous solution, gives a light green color changing to a deep emerald green when sodium acetate is added.

*Analyses.* Calc. for  $C_{20}H_{27}O_4N_2 \cdot 2HCl \cdot SnCl_4$ : C, 34.74; H, 4.24; N, 6.08. Found: C, 35.55; H, 4.47; N, 6.13.

When an aqueous suspension of the tin double salt was decomposed with hydrogen sulfide the filtrate consisted of a red solution of the aminophenol hydrochloride. Attempts made to obtain the crystalline salt failed since this proved too soluble for isolation, and manipulation was rendered difficult by the ease with which the amino group was replaced by hydroxyl under the influence of acid. In a number of instances, in which the solution stood for a long time in the refrigerator, a well-defined hydrochloride crystallized, but analysis showed this salt to be the dihydrochloride of dihydroxy-dihydroquinine. Likewise all attempts to obtain the free base were unsuccessful because of its instability.

**5,8-Dihydroxy-dihydroquinine Dihydrochloride.**—Diamino-dihydroquinine obtained from 24 g. of the *p*-sulfo-phenylazo dye was boiled with 5 parts of 1:1 hydrochloric acid for 3 hours, and the resulting deep red solution concentrated to smaller volume and chilled, rosetts of red silky needles soon filling the liquid. The salt, washed with 10% hydrochloric acid, was recrystallized from this solvent and formed rosetts of vermilion needles which were collected, washed with 10% hydrochloric acid, and air-dried. The yield was 5.5 g. The salt is easily soluble in water or alcohol, forming an orange-red solution. It is less soluble in dil. hydrochloric acid or in salt solution, and insoluble in acetone. When anhydrous, it decomposes at 208–211°. Sodium carbonate and dil. aqueous ammonia added to its solution precipitate the free base as yellow amorphous flocks which rapidly turn green on exposure to air and finally become brown. It is soluble in alkali and excess of ammonia to form brown solutions which gradually deepen in color. Ferric chloride gives a light brown color which changes to a brown-olive when sodium acetate is added. The addition of hydrobromic acid or sodium bromide to the solution of the salt causes the separation of the hydrobromide as rosetts of flat, red needles.

The salt was also obtained when acid solutions of amino-hydroxy-dihydroquinine were allowed to stand for a long time.

*Analyses.* Calc. for  $C_{20}H_{25}O_4N_2 \cdot 2HCl \cdot 4H_2O$ :  $H_2O$ , 14.31. Found:  $H_2O$ , 15.10. Calc. for  $C_{20}H_{25}O_4N_2 \cdot 2HCl$ : N, 6.49; Cl, 16.43. Found: N, 6.57; Cl, 16.25.

Because of the instability of the free base we have been unable to obtain it in crystalline form.

## B. Quinoline Derivatives

**5-Amino-6-methoxy-8-(*p*-sulfo-phenylazo)quinoline.**—Diazotized sulfanilic acid was coupled in the usual way with 5-amino-6-methoxyquinoline<sup>5</sup> in dil. acetic acid containing sufficient sodium acetate to act as buffer. A deep purple solution formed, accompanied by a tar which crystallized when alcohol was added. When dissolved in 50% alcohol with the aid of ammonia, and heated, re-acidifying the solution with acetic acid, the acid separated as flat, brown, microscopic needles which did not melt when heated to 295°. It is almost insoluble in the usual neutral solvents. The solution in dil. alkali is orange-red, and purple in dil. acids, while in conc. sulfuric acid it gives a red solution which appears purple in thin layers.

<sup>5</sup> Ref. 2, p. 2285.



*Analysis.* Calc. for  $C_{10}H_{14}O_4N_2S$ : N, 15.63. Found: N, 16.04.

**5,8-Diamino-6-methoxyquinoline.**—Thirty-two g. of the sulfo-phenylazo dye dissolved in 300 cc. of 10% ammonia were saturated with hydrogen sulfide. Decolorization occurred rapidly, with deposition of crystals of the deep olive-brown diamino base. The mixture was made distinctly ammoniacal, filtered, and washed with water. The yield was 15 g. Extraction of the mother liquor with ether gave an additional gram. Recrystallization from toluene with the addition of bone black gave lustrous golden leaflets which are fairly stable when pure, but gradually turn olive colored when moist, due to oxidation. When rapidly heated, the base darkens above  $155^{\circ}$ , sinters, and then melts at  $163\text{--}164^{\circ}$  to form a dark tar. It is appreciably soluble in acetone and chloroform, especially on warming, and in hot alcohol, benzene or toluene, and only sparingly soluble in ether, to form yellow solutions which darken to a brown-olive color on standing. The solution in dil. acid is a reddish-orange, resembling the corresponding dihydroquinine derivative, and in conc. sulfuric acid the color is a faint yellow. A concentrated solution in 10% hydrochloric acid deposits delicate yellow needles of the polyhydrochloride on chilling. The solution in dil. acetic acid turns a light green when treated with ferric chloride, changing to a deep emerald green when sodium acetate is added.

*Analysis.* Calc. for  $C_{10}H_{11}ON_2$ : N, 22.22. Found: N, 22.34.

**8-Amino-5-hydroxy-6-methoxyquinoline.**—Three g. of diamino-6-methoxyquinoline were dissolved in 30 cc. of 10% hydrochloric acid, warmed for 30 minutes on the water-bath, then diluted with water, and boiled free from air. The solution was chilled and neutralized with a considerable excess of sodium acetate solution. When rubbed the solution yielded 2 g. of the aminophenol as a yellow powder which quickly turned to an olive color on the surface because of oxidation. It was recrystallized by dissolving it in a considerable amount of hot toluene, filtering rapidly, cooling, and again filtering rapidly from green amorphous flocks which had separated. On scratching, the yellow filtrate yielded aggregates of yellow microscopic leaflets or stout crystals which darkened to an olive color when exposed to the air. It darkened above  $130^{\circ}$  and slowly melted to a dark mass at  $180\text{--}182^{\circ}$  with preliminary sintering. It is appreciably soluble in methyl alcohol, acetone, and ether, and in hot benzene or toluene. It crystallizes from hot alcohol as stout microscopic crystals and dissolves in dil. acids with the formation of an orange-red solution. Addition of ferric chloride to a solution, followed by sodium acetate, gave a deep emerald-green color. The solution in alkali, at first yellow in color, changes almost instantly to green.

*Analysis.* Calc. for  $C_{10}H_{10}O_2N_2$ : N, 14.73. Found: N, 14.60.

This compound proved to be identical with the substance obtained as follows. Fourteen g. of 5-hydroxy-6-methoxy-8-phenylazoquinoline, described below, were dissolved in 140 cc. of 10% ammonia, and hydrogen sulfide was passed in until the deep purple liquid changed to a brown, with deposition of glistening crystals of the 8-amino-5-hydroxy-6-methoxyquinoline. The yield was 6 g. Recrystallization from toluene, as previously described, gave a yellow substance which agreed in all properties with the aminophenol described above. This was confirmed by a mixed melting point determination.

*Analysis.* Calc. for  $C_{10}H_{10}O_2N_2$ : N, 14.73. Found: N, 14.63.

**5-Hydroxy-6-methoxy-8-(p-sulfo-phenylazo)quinoline.**—Because of the insolubility of the amino-azo dye described above, its conversion into the hydroxyazo dye could not be accomplished conveniently in alcoholic solution as in previous instances but was carried out as follows. Sixteen g. of the amino-azo dye were suspended in 160 cc. of hot glacial acetic acid and then 160 cc. of hot 1:1 hydrochloric acid were added. As the deep purple paste of the hydrochloride which formed was heated on the water-bath it gradually dissolved, and after 10 minutes the solution turned a deep orange-red

and deposited the hydroxyazo dye almost quantitatively. Redissolved in hot 50% alcohol with the aid of ammonia and re-acidified with hydrochloric acid it formed a purple powder which appeared under the microscope as rosets of brown platelets. It is practically insoluble in neutral solvents and does not melt when heated to 290°.

*Analyses.* Calc. for  $C_{16}H_{13}O_2N_2S \cdot H_2O$  :  $H_2O$ , 4.77. Found:  $H_2O$ , 5.51. Calc. for  $C_{16}H_{13}O_2N_2S$  : N, 11.68. Found: N, 11.78.

**5,8-Dihydroxy-6-methoxyquinoline.**—When 5 g. of diamino-methoxyquinoline were boiled for 3 hours in 1:1 hydrochloric acid and then chilled, red-brown crystals of the dihydroxy hydrochloride slowly separated. This salt was washed with the acid, dissolved in water, and treated with an excess of sodium acetate. On rubbing, 3 g. of the base quickly separated as yellow microscopic prisms which became purple on exposure. It was recrystallized from about 40 parts of alcohol and then from toluene, forming lustrous yellow leaflets and needles melting at 195–197° with slight preliminary softening and darkening. It is sparingly soluble in the cold in methyl and ethyl alcohols and in acetone, but more readily soluble if the solvent is warmed. It dissolves in dil. acids with the formation of a brown-orange colored solution and in conc. sulfuric acid with an orange-yellow color. The solution in alkali is brown and the shade deepens on standing, while an alcoholic solution gives an olive color with ferric chloride.

*Analyses.* Calc. for  $C_{16}H_9O_2N$  : C, 62.80; H, 4.71; N, 7.33. Found: C, 62.90; H, 4.72; N, 7.81.

**Action of Acids on 5,8-Diaminoquinoline.**—Two and a half g. of diaminoquinoline were boiled 3 hours with 1:1 hydrochloric acid, a portion of the hydrochloride remaining undissolved throughout. From the collected salt almost all of the base was recovered unchanged. When the mother liquor was rendered alkaline, it showed the presence of a trace of hydroxy compound by the deposition of green flocks, but the odor of ammonia was scarcely detectable on boiling.

### Summary

Like the amino groups in the amino azo dyes derived from 5-amino-dihydroquinine and 5-amino-6-methoxyquinoline, those in the 5,8-diamino-compounds obtained from the dyes by reduction are easily replaceable by hydroxyl. A number of the intermediate and end products of this transformation are described.

[CONTRIBUTION FROM THE LABORATORIES OF THE ROCKEFELLER INSTITUTE FOR MEDICAL RESEARCH]

## SYNTHESES IN THE CINCHONA SERIES. VIII. THE HYDROGENATION OF DIHYDROCINCHONINE, CINCHONINE AND DIHYDROQUININE<sup>1</sup>

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The hydrogenation of the cinchona alkaloids has been studied by many workers in the past. Since the attempts of others by different methods had yielded substances of indefinite character, Konek von Norwall,<sup>2</sup> and Lippmann and Fleissner<sup>3</sup> applied the Ladenburg method of reduction

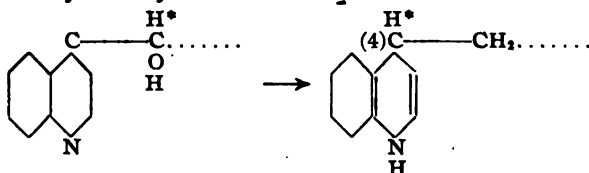
<sup>1</sup> Presented at the Annual Meeting of the American Chemical Society, New York, September, 1921.

<sup>2</sup> von Norwall, *Monatsh.*, 16, 630 (1895).

<sup>3</sup> Lippmann and Fleissner, *ibid.*, 16, 321 (1895); *Ber.*, 28, 1637 (1895); 29, 801 (1896).

with sodium and alcohol with the idea of reducing the quinoline portion of the substance. Lippmann and Fleissner obtained from quinine a strongly basic, thick oil or resin which gave the color reactions of a tetrahydroquinoline derivative but from which no crystalline compounds were obtained, with the exception of a chloroplatinate. Konek von Norwall reduced cinchonine with sodium and ethyl alcohol to an amorphous non-crystallizable substance which he believed to be a dihydrocinchonine. He subsequently substituted amyl alcohol as the solvent and then obtained a product which, although amorphous as the free base, was readily converted by nitrous acid into a crystalline salt which he described as the nitrite of a nitrosotetrahydrocinchonine. Quinine, quinidine and cinchonidine were then found to yield similar products.

In 1901 Tafel<sup>4</sup> noted that by the use of his electrolytic reduction method on the cinchona alkaloids 4 hydrogen atoms were absorbed, the product, however, being non-crystalline. More recently Freund and Bredenberg<sup>5</sup> repeated Tafel's work and obtained from cinchonine a compound in 40% yield in which one hydrogen molecule entered the quinoline nucleus, with simultaneous reduction of the secondary alcoholic group by the other. This substance was identified as a Q-dihydro-desoxycinchonine or Q-dihydrocinchonane.<sup>6</sup> A by-product of the reaction was an oily non-crystalline substance possessing the same composition and which these workers considered to be an isomer and designated as isodihydro-desoxycinchonine. With the reduction of the secondary hydroxyl group to hydrogen, the asymmetry of the carbon atom



connecting the quinoline and the quinuclidine nuclei is destroyed, while the addition of the two hydrogen atoms to the quinoline nucleus creates a new asymmetric carbon at Position 4 which would explain the production of two isomeric bases. On reduction of the crystalline base with sodium and amyl alcohol an oily tetrahydro-desoxycinchonine (tetrahydrocinchonane) was obtained which yielded on hydrogenation with palladium and hydrogen an oily hexahydrocinchonane, both bases forming crystalline salts.

A year later Skita and Brunner<sup>7</sup> succeeded in reducing the cinchona alkaloids with a large excess of platinum black and hydrogen under pressure

<sup>4</sup> Tafel, *Ber.*, **34**, 3299 (1901).

<sup>5</sup> Freund and Bredenberg, *Ann.*, **407**, 43 (1915).

<sup>6</sup> For the meaning of the suffix *-ane*, cf. *THIS JOURNAL*, **42**, 1489 (1920).

<sup>7</sup> Skita and Brunner, *Ber.*, **49**, 1597 (1916).

to high-melting crystalline hexahydro alkaloids and finally to the dodecahydro compounds. In the case of the hexahydro alkaloids, however, they make no mention of the occurrence of isomers resulting from the new asymmetry of carbon (4).

In connection with our synthetic studies in the cinchona group we were led to seek for a less costly and cumbersome method for their reduction than that devised by Skita and Brunner. Because of the rather indefinite results of Konek von Norwall and Lippmann and Fleissner, it occurred to us that, by using the dihydro alkaloids as starting material, sodium and amyl alcohol should yield products the same as those described by Skita and Brunner. To our surprise, however, dihydrocinchonine yielded an oil which was found to be a mixture of different bases. On converting this mixture into the dihydrochlorides in absolute alcoholic solution, it was found possible by fractional crystallization to isolate three different salts. The least soluble of these was obtained in about 25% yield and proved to be the dihydrochloride of a hexahydrocinchonane<sup>a</sup> which yielded a crystalline base melting at 106-7°. The most soluble salt proved also to be the dihydrochloride of a hexahydrocinchonane and was obtained in about equal amount. This salt likewise yielded a

<sup>a</sup> After this communication had been sent to the editor, papers by G. Giemsa and J. Halberkann [*Ber.*, 54, 1167, 1189 (1921)] appeared in which these authors criticize our use of the ending "ane" as a simplification of the term "desoxy" alkaloids on the ground that such a name should just as properly belong to the "still hypothetical reduction products of hydroquinene" and consequently necessitate the confusing use of prefixes  $\alpha$ -,  $\beta$ -, etc. These authors apparently have failed to realize that if Rabe's views on the stereochemical relationships of the cinchona alkaloids are correct (and they are supported by excellent evidence) the reduction of hydroquinene should yield a mixture of what we have called dihydroquinane (dihydro-desoxyquinine) and dihydroquinidane (dihydro-desoxyquinidane), a third substance being impossible. In spite of their objections to this terminology, they have applied it to their own apparently isomeric substances, designating as hydrocupreane and hydroquinane the substances prepared by them by diazotization of the 5-amino alkaloids. They justify this on the ground that their substances are produced by a method so gentle as to make unlikely the occurrence of optical isomerization in the reduction of the secondary alcoholic group to  $\text{CH}_3$ , whereas the reaction involving the use of phosphorus pentachloride for the preparation of the desoxy alkaloids over the chloro compounds is more apt to affect the steric relationship of these to the parent alkaloids.

These statements are incompatible with Rabe's views, and unless Giemsa and Halberkann's "hydrocupreane" had undergone optical or other intramolecular rearrangement it should have been identical with our dihydrocupreane. Since it has been shown to be different it must be concluded that their substances, the products of a little understood reaction, are the result of some such rearrangement.

Finally, the possibility of any isomerization with phosphorus pentachloride seems most remote since the direct reduction of dihydrocinchonine with sodium or zinc as described in this paper yields the same  $\alpha$ - and  $\beta$ -hexahydrocinchonanes as those obtained by reduction of dihydrocinchonane which was prepared over the chloro compound. We see no reason, therefore, for discontinuing the use of the terminology which we have begun.

crystalline base melting at 106–106.5°. We have designated the former base  $\alpha$ - and the latter as  $\beta$ -hexahydrocinchonane. These substances are unquestionably epimers, both being formed when carbon atom (4) of the quinoline ring becomes asymmetric, just as was assumed by Freund and Bredenberg in the electrolytic reduction of cinchonine. That these substances are tetrahydroquinoline derivatives was shown by the fact that they form stable dihydrochlorides, nitrosamines, N-acyl derivatives and phenylazo dyes, the last of which was obtained in crystalline form only in the case of the  $\alpha$ -compound. They also give the characteristic color reactions of tetrahydroquinoline with ferric chloride.

It appeared rather surprising that the reduction of the secondary alcoholic group of cinchonine to the  $\text{CH}_2$  group should have occurred here as well as in the electrolytic reduction. To prove the correctness of the findings, however, dihydrocinchonine was converted through the chloro compound into dihydrocinchonane, which was in turn reduced with sodium and amyl alcohol;  $\alpha$ - and  $\beta$ -hexahydrocinchonane were obtained exclusively. One of these isomers must therefore be the hexahydro-desoxycinchonine described by Freund and Bredenberg but not obtained by them in crystalline form.<sup>9</sup>

The third substance obtained by fractionation of the hydrochlorides was isolated finally as a dihydrobromide. Its elementary composition corresponds to that of a hexahydrocinchonine. Unfortunately, the base could not be obtained crystalline and could not, therefore, be compared with the product of Skita and Brunner. We are, however, of the opinion that our substance is different from theirs. From our experience and that of Freund and Bredenberg, it is rather strange that Skita and Brunner did not observe the formation of epimeric isomers in the reduction of the alkaloids by their method. Our third substance also gives all of the reactions of a tetrahydroquinoline. Under the conditions employed it would seem, therefore, that the alcoholic group does not suffer reduction in all of the alkaloid used.

To ascertain whether other reducing agents would yield the same compounds, dihydrocinchonine was reduced with zinc and hydrochloric acid; this process yielded an oily base from which an appreciable amount of  $\alpha$ -hexahydrocinchonane was isolated by means of the hydrochloride. Since the yield of this product was much poorer than that obtained by the sodium method, the reaction unquestionably proceeded partly in a different sense.

<sup>9</sup> Since a tetrahydrocinchonane (tetrahydro-desoxycinchonine) which they also describe was found by them to possess  $[\alpha]_D$  64.6°, this substance must therefore be isomeric with the tetrahydrocinchonane prepared by us by the reduction of cinchonine and which is described further on. This base gave  $[\alpha]_D$  209.0°. Accordingly, our  $\beta$ -base should belong to the series of compounds which these workers obtained from their crystalline dihydrocinchonane and should therefore be the same as their amorphous hexahydro-desoxycinchonine. Unfortunately, they did not describe its rotation.

It was then of interest to repeat the experiments of Koněk von Norwall with cinchonine itself. Here, also, a viscous sirup was obtained which was likewise found to be a mixture. By conversion into the hydrochloride a crystalline fraction was obtained with little difficulty which yielded a crystalline base melting at 116.5–117.5° and with practically the same rotation given by  $\alpha$ -hexahydrocinchonane. This base proved to be  $\alpha$ -tetrahydrocinchonane, since on reduction with palladium and hydrogen it yielded the  $\alpha$ -hexahydro base. From the mother liquor of the above salt it was found difficult to isolate any other products of the reduction. A clue to their nature was found, however, by reducing the residue with palladium and hydrogen, a process which could reduce only the vinyl side-chain. From the resulting mixture the hydrochlorides of  $\alpha$ - and  $\beta$ -hexahydrocinchonane and hexahydrocinchonine dihydrobromide were readily isolated, showing that the original reduction mixture contained besides  $\alpha$ -tetrahydrocinchonane,  $\beta$ -tetrahydrocinchonane and tetrahydrocinchonine. The so-called nitroso-tetrahydrocinchonine nitrite described by Koněk von Norwall was therefore probably a mixture and not solely, if at all, a derivative of tetrahydrocinchonine.

Finally dihydroquinine was also reduced by this method, but curiously enough the only substance which could be isolated in pure crystalline form and in fair yield was the dihydrochloride of hexahydroquinine. The nature of this salt was established by the preparation of a nitroso and monobenzoyl derivative and the usual color reactions. The base unfortunately could not be obtained in crystalline form.

### Experimental Part

#### A. Reduction of Dihydrocinchonine (Cinchotine)

100 g. of dihydrocinchonine were dissolved in 2 kg. of boiling dry amyl alcohol and reduced at the boiling temperature with 150 g. of sodium. The reaction required in all from 4 to 6 hours. When the practically colorless solution was treated with water and the amyl alcohol removed with steam, a resinous residue remained which was extracted with ether. Concentration of the dried ethereal solution left an amber colored oil which was dissolved in 1 liter of absolute alcohol. A solution of hydrochloric acid in absolute alcohol was added until the reaction became acid to congo red. A copious crop of microscopic needles gradually separated and was collected and washed with cold, acidulated absolute alcohol, forming a faintly bluish-purple mass which weighed 50 g. when dry. Recrystallization from 3 parts of boiling water gave a crop of almost flat, minute, colorless needles which, after they had been washed with ice water and dried, weighed 16 g. and proved to be practically pure  $\alpha$ -hexahydrocinchonane dihydrochloride. The aqueous mother liquor, concentrated to 75 cc., gradually deposited a second crop of crystals, which, on recrystallization from a small volume of water, yielded 7 g. of the characteristic flat needles of the salt of the  $\alpha$ -compound. The mother liquors treated in a similar manner finally gave an additional 5 g., or 28 g. in all.

When the aqueous mother liquor from the last fraction was concentrated to about 50 cc. and treated with an equal volume of 40% hydrobromic acid a hydrobromide crystallized rapidly. Under the microscope, it was found to consist mainly of 6-sided elongated plates and prisms of the salt of hexahydrocinchonine, mixed with small, com-

pect prisms of the hydrobromide of  $\beta$ -hexahydrocinchonane, which was easily removed by recrystallization. The yield of the mixed salt was 17 g.

The original alcoholic mother liquor from which the first crude fraction had been obtained was concentrated *in vacuo* to a sirup and dissolved in about 150 cc. of absolute alcohol. On standing in the refrigerator the solution, which had deepened considerably in color, slowly deposited a hard, compact crust of pyramided rhombs which were filtered off after 3 or 4 days and washed with cold absolute alcohol. This fraction weighed 32 g. and consisted mainly of  $\beta$ -hexahydrocinchonane dihydrochloride. The mother liquor from this fraction, concentrated to small bulk and allowed to stand in the refrigerator for several weeks, gave a further slow deposit of crystals, but this fraction was obviously a mixture, and the amount too small to make its study profitable.

**$\alpha$ -Hexahydrocinchonane.**—When the hydrochloride of the  $\alpha$ -base first described was dissolved in water and treated with an excess of alkali, a colorless gum was obtained which was easily extracted with ether. The dried extract, on concentration, left an almost colorless sirup which crystallized on standing. When this material was dissolved in sufficient hot ligroin and seeded after it cooled, the base separated as a hard crust of rhombic plates and flat prisms. After repeated recrystallization from ligroin and finally from a small volume of alcohol, and cooling to 0°, the base melted sharply at 106–107° (corr.). Although colorless at first the  $\alpha$ -base rapidly turns amber colored on the surface when exposed to sunlight; but when kept in brown glass containers it remains colorless. It is readily soluble in organic solvents, except ligroin which, however, dissolves it appreciably. The base yields stable di-acid salts, solutions of which give an olive-green color with ferric chloride and an emerald-green color with permanganate. It couples slowly with diazotized sulfanilic acid to form a red solution of the salt of the azo dye.  $[\alpha]_D^{25}$  is 212–217° in absolute alcohol,  $c = 1.123$  (g. of substance per 100 cc. of solvent).

**Analyses.** Calc. for  $C_{19}H_{23}N_3$ : C, 80.23; H, 9.86; N, 9.86. Found: C, 80.10; H, 9.63; N, 10.05.

**THE DIHYDROCHLORIDE.**—This salt is readily purified by recrystallization from water; it forms characteristic long, flat, colorless, glistening needles which darken slightly but do not melt when heated to 285°. It is fairly soluble in water, especially on warming, and very difficultly so in cold absolute alcohol, although the hot solvent dissolves it more readily. Hydrochloric acid or sodium chloride salts it out of a not too dilute aqueous solution. Strong hydrobromic acid likewise precipitates the dihydrobromide as long, flat needles which resemble the hydrochloride. The aqueous solution of the salt is acid to litmus, but not to congo red.  $[\alpha]_D^{24}$  is 69.2° in water;  $c = 1.026$ .

**Analyses.** Calc. for  $C_{19}H_{23}N_3 \cdot 2HCl$ : C, 63.83; H, 8.41; N, 7.84; Cl, 19.85. Found: C, 63.60; H, 8.23; N, 8.04; Cl, 19.75.

**N-Nitroso- $\alpha$ -hexahydrocinchonane Hydrochloride.**—A conc. aqueous solution of the dihydrochloride was treated with a slight excess of a conc. solution of sodium nitrite, yielding a yellow gum which crystallized rapidly when it was rubbed. Since purification of the hydrochloride by simple recrystallization was made difficult because of contamination with the sparingly soluble nitrite of the nitroso compound, the collected salt was dissolved in water and the nitroso base precipitated with alkali and extracted with ether. The washed ether was shaken with a slight excess of dil. hydrochloric acid and the hydrochloride was isolated from the resulting solution by concentration *in vacuo*. Recrystallized from a small volume of water containing a little hydrochloric acid, the hydrochloride separates as flat, lustrous, cream colored needles which melt and effervesce at 203–205°. It is easily soluble in alcohol, quite readily in water, and much less so in dilute hydrochloric acid or salt solution. It gives the Liebermann reaction.  $[\alpha]_D^{27}$  is + 68.0° in water;  $c = 1.000$ . Alkali precipitates the base as a gum which is easily soluble in ether and could not be made to crystallize.

*Analyses.* Calc. for  $C_{18}H_{21}ON_2.HCl$ : N, 12.00; Cl, 10.14. Found: N, 12.15; Cl, 10.13.

**N-Acetyl- $\alpha$ -hexahydrocinchonane Hydrochloride.**—Two g. of the  $\alpha$ -base were dissolved in 10 cc. of benzene, treated with 1 cc. of acetic anhydride and boiled for several minutes, until the benzene boiled away. A small volume of absolute alcohol was added and then alcoholic hydrochloric acid until the solution was acid to congo red. On the addition of several volumes of dry ether the hydrochloride gradually crystallized. Reprecipitated with ether from a concentrated alcoholic solution, the salt formed colorless microscopic leaflets which melted at 235–237° with slight preliminary softening. It dissolves easily in water or alcohol and very sparingly in acetone. Contrary to the unacylated base, it no longer couples with diazo compounds and gives no color with ferric chloride or permanganate.  $[\alpha]_D^{27}$  is +37.0° in water;  $c = 1.000$ . Alkali precipitates the base as a gum which dissolves easily in ether, but could not make it crystallize.

*Analyses.* Calc. for  $C_{21}H_{29}ON_2.HCl$ : N, 7.73; Cl, 9.78. Found: N, 7.65; Cl, 9.56.

**N-Benzoyl- $\alpha$ -hexahydrocinchonane Hydrochloride.**—One and a half g. of the  $\alpha$ -base dissolved in 25 cc. of dry acetone were treated with 1 cc. of benzoyl chloride. The solution warmed slightly and deposited a trace of a precipitate. The filtrate was concentrated to a small volume, acidified with alcoholic hydrochloric acid, and then treated with dry ether to incipient turbidity. The crystallization which ensued on rubbing the vessel was aided by the occasional addition of more ether. Recrystallized from methyl ethyl ketone, the salt separated slowly as colorless microscopic platelets which sinter at about 175° and slowly melt at 215–220°. The salt is easily soluble in water or alcohol.  $[\alpha]_D^{27} = +13.0^\circ$  in water;  $c = 0.384$ . The free base was obtained from the salt as a colorless gum which could not be made to crystallize.

*Analyses.* Calc. for  $C_{28}H_{39}ON_2.HCl$ : N, 6.59; Cl, 8.35. Found: N, 6.78; Cl, 8.29.

**6-Phenylazo- $\alpha$ -hexahydrocinchonane.**—Half a gram of aniline dissolved in 15 cc. of *N* hydrochloric acid was diazotized with 5 cc. of *N* sodium nitrite and added to a chilled solution of 1.9 g. of the  $\alpha$ -dihydrochloride in 25 cc. of water. Fifteen cc. of 20% sodium acetate were then added, causing the separation of a reddish-orange gum, presumably mostly a diazo-amino compound. An equal volume of alcohol was added and, when solution was complete, this was followed by sufficient strong hydrobromic acid to form a deep purple-red solution which deepened in color on standing. After the solution had stood for 24 hours at room temperature, the removal of the alcohol *in vacuo* caused the separation of a deep red tar which changed when rubbed with water to a purple mass of microscopic needles. The separation was aided by the addition of sodium bromide. The collected salt was dissolved in warm 50% alcohol and made alkaline with sodium hydroxide, which caused the purple-red solution to change to a brown-orange color and deposit the dye base as lustrous orange colored leaflets. The yield was 0.7 g. Recrystallized from 85% alcohol it forms rosetts of thin, rounded platelets which melt at 153–156°. The dye is very readily soluble in benzene and in chloroform and easily in the other solvents except ligroin. It dissolves in dil. acids with a deep red color, purplish-pink in thin layers, while the solution in conc. sulfuric acid shows a deep brown-red hue which appears light olive-green in thin layers.

*Analysis.* Calc. for  $C_{28}H_{33}N_3$ : N, 14.43; Found: N, 14.65.

**$\beta$ -Hexahydrocinchonane.**—The free base was obtained from the pure hydrochloride described below as a colorless oil which crystallized on standing. Recrystallized from ligroin, it forms lustrous rhombic plates which, after a final recrystallization from alcohol with the aid of a freezing mixture, melt at 106–106.5°, or at about the same point as the  $\alpha$ -base. However, a mixture of both bases melts 15–20° lower. Contrary to the action of the  $\alpha$ -base, the  $\beta$ -compound remains colorless on exposure to sunlight. Its salts give



the same color reactions as those of the  $\alpha$ -base with ferric chloride, with permanganate, and with diazotized sulfanilic acid. It is readily soluble in organic solvents with the exception of ligroin.  $[\alpha]_D^{25}$  is  $18.15^\circ$  in absolute alcohol;  $c=0.992$ .

*Analyses.* Calc. for  $C_{19}H_{23}N_2$ : C, 80.23; H, 9.86; N, 9.86. Found: C, 79.90; H, 10.02; N, 9.77.

**THE DIHYDROCHLORIDE.**—The crude salt (32 g.) previously described as the second fraction (p. 1084) was readily purified by recrystallization from water. It separates slowly as a hard crust of rhombs and pyramidal prisms which occasionally measured 5 mm. in diameter and contain 1 molecule of water of crystallization. When heated rapidly to  $230^\circ$  and then slowly, the salt melts at  $237\text{--}240^\circ$  to a liquid filled with bubbles. It is readily soluble in water, appreciably so in alcohol, and insoluble in acetone or in ether. The aqueous solution reacts acid to litmus, but neutral to congo red.  $[\alpha]_D^{25}$  is  $84.0^\circ$  in water;  $c=1.000$ .

*Analyses.* Calc. for  $C_{19}H_{23}N_2 \cdot 2HCl \cdot H_2O$ :  $H_2O$ , 4.80. Found: 4.54. Calc. for  $C_{19}H_{23}N_2 \cdot 2HCl$ : N, 7.84; Cl, 19.85. Found: N, 8.07; Cl, 19.68.

**Nitroso- $\beta$ -hexahydrocinchonane and its Hydrochloride.**—As in the case of the  $\alpha$ -salt, the  $\beta$ -hydrochloride yielded the hydrochloride of the nitroso compound, which was purified by recrystallization from water with the addition of hydrochloric acid. The base obtained from the salt formed an amber colored oil which crystallized on standing. When allowed to separate slowly from ligroin, it forms long, prismatic, cream colored needles which melt at  $92.5\text{--}93.5^\circ$  (corr.). It is readily soluble in organic solvents and gives the Liebermann reaction.  $[\alpha]_D^{25}$  is  $107.0^\circ$  in absolute alcohol;  $c=1.000$ .

*Analysis.* Calc. for  $C_{19}H_{27}ON_2$ : N, 13.41. Found: N, 13.76.

The salt isolated above forms glistening, cream colored leaflets which contain 1 molecule of water of crystallization and melt with effervescence at  $209\text{--}211^\circ$ . It is sparingly soluble in cold water, more readily in alcohol and very sparingly in acetone.  $[\alpha]_D^{25}$  is  $68.4^\circ$  in water;  $c=0.746$ .

*Analyses.* Calc. for  $C_{19}H_{27}ON_2 \cdot HCl \cdot H_2O$ :  $H_2O$ , 4.90. Found: 4.87. Calc. for  $C_{19}H_{27}ON_2 \cdot HCl$ : N, 12.00; Cl, 10.14. Found: N, 12.36; Cl, 10.28.

**N-Benzoyl- $\beta$ -hexahydrocinchonane Hydrochloride.**—One and a half g. of the  $\beta$ -base dissolved in 25 cc. of dry acetone were treated with 1 cc. of benzoyl chloride. After 15 minutes the clear solution was treated with dry ether and rubbed until the salt crystallized. Recrystallized from methyl ethyl ketone, it forms aggregates of colorless needles which melt at  $232\text{--}234^\circ$  and are easily soluble in water.  $[\alpha]_D^{27}$  is  $95.0^\circ$  in water;  $c=1.000$ .

*Analyses.* Calc. for  $C_{26}H_{33}ON_2 \cdot HCl$ : N, 6.59; Cl, 8.35. Found: N, 6.86; Cl, 8.47.

**Hexahydrocinchonine Dihydrobromide.**—This salt was obtained as previously described (p. 1084) by the addition of hydrobromic acid to the aqueous mother liquors from the  $\alpha$ -dihydrochloride. The crude hydrobromide (17 g.) was recrystallized repeatedly from small volumes of water until the optical rotation became constant. It then formed characteristic long, lustrous, faintly violet, hexagonal plates and prisms which sinter and darken slightly, but do not melt below  $290^\circ$ . The salt is quite readily soluble in water and very sparingly in alcohol.  $[\alpha]_D^{27}$  is  $50.0^\circ$  in water;  $c=1.000$ . It gives the same color reactions with ferric chloride, with permanganate and with diazotized sulfanilic acid as the salts of the  $\alpha$ - and  $\beta$ -bases. Its aqueous solution reacts acid to litmus, but neutral to congo red, and yields a nitrosamine with sodium nitrite. Alkali precipitates the free base as a gum which, so far, has failed to crystallize.

*Analyses.* Calc. for  $C_{19}H_{23}ON_2 \cdot 2HBr$ : C, 49.35; H, 6.55; N, 6.06; Br, 34.63. Found: C, 49.65; H, 6.51; N, 6.34; Br, 34.72.

**Reduction of Dihydrocinchonine with Zinc and Hydrochloric Acid.**—Twenty g. of dihydrocinchonine were dissolved in 400 cc. of 1:1 hydrochloric acid, and the solution was boiled and treated gradually with 40 g. of granulated zinc (30 mesh). When the zinc was dissolved, water was added to redissolve the pasty double salt which separated as the mixture cooled, and then an excess of ammonia was added. The dried ether extract was concentrated and yielded a yellow oil which was dissolved in 100 cc. of absolute alcohol and treated with dry hydrogen chloride until acid to congo red. When seeded with  $\alpha$ -hexahydrocinchonane dihydrochloride, rapid crystallization occurred which was completed in the refrigerator. The dried salt weighed 3 g., or much less in proportion to the yield obtained by the sodium reduction. It proved identical with the salt of the  $\alpha$ -base previously isolated. In all probability the  $\beta$ -base is to be found in the mother liquors from the  $\alpha$ -hydrochloride, but the poor yield and its solubility rendered its isolation difficult.

## B. Reduction of Dihydrocinchonane

Eighteen g. of dihydrocinchonane hydrochloride (see below) were converted into the base and the dried ether extract concentrated to a sirup. This was dissolved in 320 g. of amyl alcohol and reduced with 24 g. of sodium. After removal of the amyl alcohol, the ether extract yielded a colorless oil which was dissolved in 160 cc. of absolute alcohol and made acid to congo red by dry hydrogen chloride. Thus 10.5 g. of a salt corresponding to that of  $\alpha$ -hexahydrocinchonane was obtained. On conversion of this into the free base, an oil was obtained which crystallized readily when seeded with  $\alpha$ -hexahydrocinchonane. Recrystallized from ligroin, it formed rhombic plates and prisms which melted at 106–107° (corr.). When mixed with the previously described  $\alpha$ -base no change in melting point occurred.  $[\alpha]_D^{26}$  is 213.0° in absolute alcohol;  $c=1.000$ .

*Analysis.* Calc. for  $C_{19}H_{23}N_2$ : N, 9.86. Found: N, 9.98.

When the mother liquor of the  $\alpha$ -hydrochloride was concentrated, 6 g. of stout prisms characteristic of the  $\beta$ -dihydrochloride were obtained. The base liberated from this salt melted at 106–106.5° (corr.). No change in melting point was observed when it was mixed with the  $\beta$ -hexahydrocinchonane previously described.  $[\alpha]_D^{26}$  is 18.7° in absolute alcohol;  $c=1.016$ .

*Analysis.* Calc. for  $C_{19}H_{23}N_2$ : N, 9.86. Found: N, 9.94.

From the mother liquors from the above salts none of the characteristic hexagonal plates of the dihydrobromide of hexahydrocinchonine could be separated.

The dihydrocinchonane used above was obtained as follows.

**Chloro-dihydrocinchonine and its Hydrochloride.**—Sixty-nine g. of dry dihydrocinchonine dihydrochloride were suspended in dry chloroform and poured in a thin stream, with cooling, into a suspension of 115 g. of phosphorous pentachloride in the same solvent. After the mixture had been warmed to 40–50° for several days, it was decomposed with ice and water, and the base liberated from the aqueous extract with alkali and extracted with ether. The oily residue was dissolved in absolute alcohol and neutralized with alcoholic hydrochloric acid. This caused the *hydrochloride* to separate as aggregates of microscopic needles. The mother liquor yielded an additional amount on addition of dry ether, or 43 g. in all. When recrystallized from 85% alcohol it forms radiating aggregates of microscopic needles and narrow leaflets which turn olive colored when heated and melt slowly at 227–228°. It is difficultly soluble in cold water and alcohol, but readily on boiling.  $[\alpha]_D^{23}$  is 48.8° in water;  $c=1.107$ .

*Analyses.* Calc. for  $C_{19}H_{23}N_2Cl.HCl$ : N, 7.98; Cl, 10.09. Found: N, 8.09; Cl, 10.04.

On treating the aqueous solution of the salt with sodium carbonate, an oil formed which crystallized when it was seeded with crystals obtained from a preliminary ethereal

extract. Dissolved in acetone and treated with water to incipient turbidity the hydrate of the base separated slowly as rhombs which contained 1.5 molecules of water of crystallization. It softens above  $55^{\circ}$  and is completely melted to a turbid liquid at  $70^{\circ}$ . Dried in a desiccator, the hydrate lost its crystalline structure. It is easily soluble in organic solvents.  $[\alpha]_D^{24}$  is  $36.4^{\circ}$  in absolute alcohol;  $c = 1.001$ .

*Analyses.* Calc. for  $C_{19}H_{22}N_2Cl \cdot 1.5H_2O$ :  $H_2O$ , 7.91; N, 8.20. Found:  $H_2O$ , 7.83; N, 8.32.

**Dihydrocinchonane and its Hydrochloride.**—Thirty-six g. of chlorodihydrocinchonine hydrochloride were reduced as in the case of dihydroquinane.<sup>10</sup> The base was obtained at first as an oil which was dissolved in absolute alcohol and treated with dry hydrogen chloride until it was neutral to moist litmus, the salt separating rapidly as glistening platelets. These were washed with a little absolute alcohol and then with dry acetone, until all the yellow color due to picric acid had been removed. Yield, 22 g. When crystallized from absolute alcohol the hydrochloride forms narrow, glistening plates and prisms which turn yellow and melt slowly at  $197$ – $199^{\circ}$  to a liquid containing bubbles. It is quite soluble in absolute alcohol, very readily in dry methyl alcohol and chloroform, and difficultly in acetone.  $[\alpha]_D^{25}$  is  $69.3^{\circ}$  in water;  $c = 1.068$ .

*Analyses.* Calc. for  $C_{19}H_{24}N_2 \cdot HCl$ : N, 8.85; Cl, 11.19. Found: N, 9.04; Cl, 11.38.

On treating a solution of the salt in 50% alcohol with an excess of sodium carbonate and diluting with water, the hydrate of the base crystallized slowly. When dissolved in acetone and treated with water to incipient turbidity, the hydrate separated as rhombs, hexagonal prisms and diamond-shaped platelets which retained 2 molecules of water of crystallization after they had been dried to constant weight in air saturated with water vapor. It is easily soluble in organic solvents and melts at  $59.5$ – $60^{\circ}$  (corr.). When it is dried in a desiccator or in dry air it loses its crystalline character.  $[\alpha]_D^{30}$  is  $113.8^{\circ}$  in absolute alcohol;  $c = 1.014$ .

*Analyses.* Calc. for  $C_{19}H_{24}N_2 \cdot 2H_2O$ :  $H_2O$ , 11.39; C, 72.10; H, 8.16; N, 8.86. Found:  $H_2O$ , 11.17; C, 72.42; H, 8.16; N, 9.17.

### C. Reduction of Cinchonine

Fifty g. of cinchonine, which had been purified by recrystallization of the sulfate and then of the base from 50% alcohol, were reduced in 1 kg. of amyl alcohol with 75 g. of sodium. On concentration, the ethereal extract yielded an amber colored oil which was dissolved in 150 cc. of absolute alcohol and made acid to congo red by the addition of dry hydrogen chloride. On standing in the refrigerator, the almost colorless solution became deep red-brown and deposited colorless needles which were collected and washed with cold absolute alcohol. The yield was 12.5 g.

**$\alpha$ -Tetrahydrocinchonane.**—On converting the above salt as usual into the base an oil was obtained which partially crystallized on standing. When the mixture was dissolved in hot ligroin, cooled, and seeded, a gradual deposition of the base occurred. A second recrystallization from ligroin yielded stout cream colored prisms which melted at  $116.5$ – $117.5^{\circ}$  (corr.) and were readily soluble in organic solvents, except ligroin.  $[\alpha]_D^{31}$  is  $209.0^{\circ}$  in absolute alcohol,  $c = 1.000$ , a value practically the same as the specific rotation of  $\alpha$ -hexahydrocinchonane. The solution of its hydrochloride gives the same color reactions as the latter with ferric chloride, permanganate and diazotized sulfanilic acid.

*Analyses.* Calc. for  $C_{19}H_{26}N_2$ : C, 80.80; H, 9.29; N, 9.93. Found: C, 81.25; H, 9.24; N, 9.90.

To establish its relationship to  $\alpha$ -hexahydrocinchonane, the tetrahydro compound

<sup>10</sup> THIS JOURNAL, 42, 1492 (1920).

was reduced in dil. acetic acid with palladium black and hydrogen.  $\alpha$ -Hexahydrocinchonane was isolated from the resulting solution.

Since the products contained in the mother liquor from the crude  $\alpha$ -tetrahydrocinchonane dihydrochloride proved too soluble for separation, a clue to the nature of the main products of the reduction was obtained by reduction with palladium and hydrogen. The mother liquor was accordingly concentrated to remove alcohol and the residue dissolved in 200 cc. of water, a solution of 0.1 g. of palladium chloride added and the mixture reduced with hydrogen. When absorption was complete, the filtrate was concentrated to dryness *in vacuo*, redissolved in absolute alcohol, concentrated again, and the process repeated to remove all water. On dissolving the residue in 200 cc. of absolute alcohol it crystallized rapidly, and yielded 10 g. of hydrochloride which on fractional recrystallization from water gave 3 g. of the characteristic crystals of  $\alpha$ -hexahydrocinchonane dihydrochloride. This would indicate that the original separation of the hydrochloride of  $\alpha$ -tetrahydrocinchonane from the other products of the reduction of cinchonine had been incomplete.

On treatment with hydrobromic acid the aqueous mother liquor from the  $\alpha$ -dihydrochloride yielded the 6-sided platelets of hexahydrocinchonine dihydrobromide.

The alcoholic mother liquor from the above hydrochlorides gave, on concentration, a copious crystallization of  $\beta$ -hexahydrocinchonane dihydrochloride.

#### D. Reduction of Dihydroquinine

Sixty g. of dihydroquinine, recrystallized from toluene,<sup>11</sup> were reduced as in previous cases with sodium in amyl alcohol. After removal of the latter, an oily base was obtained by extraction with ether. This was dissolved in 200 cc. of absolute alcohol, cooled, and made acid to congo red by passing dry hydrogen chloride through it. A small test portion of the solution was partially precipitated with ether. The gummy precipitate was dissolved in a little absolute alcohol and then ether was added cautiously, causing crystallization to occur gradually. When the main solution was seeded and kept at room temperature (gelatinization occurred in the refrigerator), a copious separation of hair-like needles and denser crystals occurred. After washing with a little absolute alcohol the salt weighed 29 g. The mother liquors from this salt, treated with ether and allowed to stand, yielded a small quantity of fibrous needles which appeared to be the salt of a different base. The quantity of this substance at our disposal and pressure of other work prevented the completion of the study of this fraction and other substances contained in the mother liquors.

**Hexahydroquinine Dihydrochloride.**—To recrystallize the above first fraction it was dissolved in the minimum amount of boiling methyl alcohol, cooled, and treated with dry ether. The crystals thus formed were recrystallized until the optical rotation had become constant, yielding about 15 g. of optically pure salt. It formed practically colorless rhombic plates which melted at 271–273° with gas evolution and preliminary softening. Although readily soluble in ordinary boiling methyl and ethyl alcohols, the salt is rather sparingly soluble in the dry solvents and almost insoluble in dry acetone and chloroform. It dissolves easily in water, and the solution gives with ferric chloride an emerald-green color which changes to an orange color on long standing.  $[\alpha]_D^{25.5}$  is  $-36.5^\circ$  in water;  $c=1.067$ . Sodium bromide salts out the *dihydrobromide* as lustrous plates. Attempts to obtain the free base in crystalline form were unsuccessful.

**Analyses.** Calc. for  $C_{20}H_{20}O_2N_2 \cdot 2HCl$ : C, 59.52; H, 8.00; N, 6.95; Cl, 17.59. Found: C, 59.68; H, 7.92; N, 7.10; Cl, 17.60.

<sup>11</sup> In an experiment in which a less pure product was used considerable charring occurred.

**N-Nitroso-hexahydroquinine Hydrochloride.**—A solution of the salt in 3 parts of water and a few drops of acetic acid was treated in the cold with a slight excess of sodium nitrite. The hydrochloride soon crystallized as radiating masses of delicate needles which changed on standing to glistening, pale yellow rhombs and prisms which were recrystallized twice from water containing a little hydrochloric acid. It turns lemon-yellow when heated, melts at  $212-213^{\circ}$  with decomposition, and is fairly soluble in water and alcohol, especially on boiling. It gives the Liebermann reaction and its aqueous solution is not changed at once by permanganate or ferric chloride.  $[\alpha]_D^{31}$  is  $-85.1^{\circ}$  in water;  $c=1.034$ .

*Analyses.* Calc. for  $C_{20}H_{27}O_2N_2.HCl$ : N, 10.62; Cl, 8.96. Found: N, 10.76; Cl, 8.92.

**N-Benzoyl-hexahydroquinine.**—The dried sirupy base from 4.1 g. of hexahydroquinine dihydrochloride was treated with 15 cc. of benzoyl chloride and heated on the water-bath for 1 hour, after which benzene was added and the solution treated with very dilute hydrochloric acid and ice. A gum separated which gradually dissolved when the mixture was shaken and ether was added to facilitate the process. The aqueous layer was then covered with ether, treated with ice and a slight excess of alkali, and quickly shaken out. The dried ethereal extract left a viscous oil which crystallized after several days. Dissolved in hot ligroin, then cooled and seeded, the base formed lustrous platelets which were purified by solution in a little benzene and addition of ligroin. It melts at  $160-160.5^{\circ}$  with slight preliminary softening and is soluble in the usual solvents, except ligroin. It does not give a color with ferric chloride.  $[\alpha]_D^{26}$  is  $-115.2^{\circ}$  in absolute alcohol;  $c=1.088$ .

*Analyses.* Calc. for  $C_{27}H_{34}O_2N_2$ : C, 74.61; H, 7.89; N, 6.45. Found: C, 74.81; H, 8.12; N, 6.69.

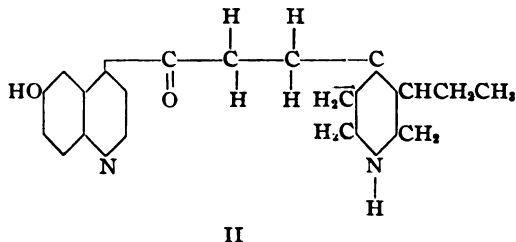
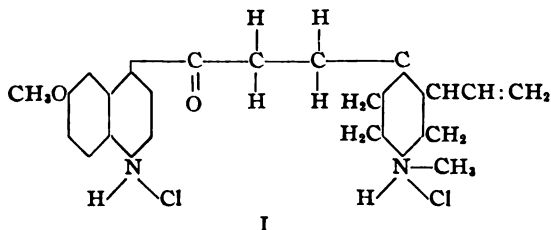
### Summary

Reduction of dihydrocinchonine with sodium and amyl alcohol yielded a mixture of hexahydrocinchonine and two epimeric hexahydrocinchonanes in the last of which the alcoholic group, as well as the quinoline ring, had suffered reduction. These two bases were also obtained by reduction of dihydrocinchonane. The relationships of these compounds to those obtained by reduction with zinc, and by the reduction of cinchonine were worked out, and necessary intermediates and derivatives described. Dihydroquinine was also reduced, yielding mainly a hexahydroquinine.

**SYNTHESES IN THE CINCHONA SERIES. IX. CERTAIN QUINICINE AND BENZOYLCINCHONA SALTS, CRYSTALLINE ETHYL DIHYDROCUPREINE (OPTOCHIN) BASE, AND OTHER DERIVATIVES<sup>1</sup>**

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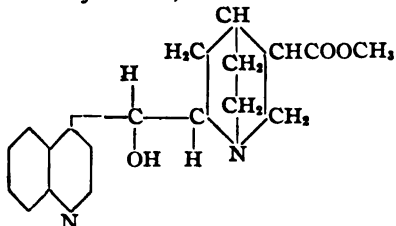
Very few quinine (quinotoxine) bases or salts have been obtained crystalline up to the present, and recourse has usually been had to the oxalate or some similar salt if a crystalline compound was indeed obtained. In nearly every case investigated by us, however, either the monohydrochloride<sup>2</sup> or the dihydrochloride could be made to crystallize with little difficulty under suitable conditions, and in the exceptions noted the neutral sulfate or hydrobromide crystallized readily. Of these salts, besides dihydroquinine sulfate, already studied by Hesse,<sup>3</sup> there are described in the present paper N-methyl-quinine dihydrochloride (I), N-methyl-dihydroquinine hydrochloride, N-ethyl-quinine hydrochloride, N-ethyl-dihydroquinine hydrochloride, N-benzyl-dihydroquinine hydrochloride, ethyl-dihydrocupreine (optotoxin) sulfate, and dihydrocupreine hydrobromide, a salt of a new quinine, (II)



<sup>2</sup> Hesse, *Ann.*, 241, 273 (1887).

corresponding to dihydrocupreine and dihydrocupreidine.<sup>4</sup> Also in the quinicine series there are described the salts of two glycine derivatives in which the NH group of the piperidine nucleus has been condensed with chloro-acetyl derivatives of aromatic amines.

We have also described benzoyl-cinchonidine dihydrochloride, benzoyl-dihydrocinchonidine hydrochloride, benzoyl-quinine dihydrochloride, and benzoyl-dihydroquinine hydrochloride which, as far as we know, are new. Cinchotenine methyl ester,



cinchotenine ethyl ester hydrochloride, and cupretenine (quitenol) methyl ester dihydrochloride, we also believe have not been described.

Hitherto only crystalline salts of ethyl dihydrocupreine (optochin) have been prepared,<sup>5</sup> and Giemsa and Halberkann report their inability to crystallize the base. It was found, however, that after the initial crystals had been obtained by spontaneous evaporation of a toluene solution, the base could readily be obtained crystalline by seeding concentrated solutions in this solvent, separating as irregular leaflets containing toluene of crystallization, at least a part of which is retained on air drying.

Finally, the ethyl bromides of dihydroquinine and ethyl-dihydrocupreine are described, as well as the dihydrobromide of hydrobromocupreine (or hydrobromo-apoquinine), and existing data on hydrobromocinchonidine are completed.

## Experimental<sup>6</sup>

### A. Quinicine Salts

**Dihydroquinicine Sulfate.**<sup>7</sup>—Dihydroquinicine was prepared from dihydroquinine<sup>8</sup> sulfate according to v. Miller, Rohde and Fussenegger<sup>9</sup> and the crude, oily base neutralized to wet litmus in absolute alcohol with 30% aqueous sulfuric acid and treated with dry ether until the initial turbidity just redissolved. The salt separated on rubbing, and was recrystallized by dissolving in hot 95% alcohol, cooling, adding an equal volume of acetone, seeding and letting stand in the cold. It has the properties mentioned by Hesse, and in addition, comes to equilibrium in the air with 3 molecules of water of crys-

<sup>4</sup> THIS JOURNAL, 41, 821, 827 (1919).

<sup>5</sup> *Ibid.*, 41, 824 (1919). Giemsa and Halberkann, *Ber.*, 51, 1332 (1918).

<sup>6</sup> Melting points and optical rotations were determined as in previous papers.

<sup>7</sup> Not fully described by Hesse, Ref. 3.

<sup>8</sup> THIS JOURNAL, 41, 819 (1919). Ger. pat. 252,136.

<sup>9</sup> v. Miller, Rohde and Fussenegger, *Ber.*, 33, 3228 (1900).

tallization (or its equivalent). When anhydrous, it gives  $[\alpha]_D^{21.5} -8.3^\circ$  in water,  $c=0.968$ , and softens and turns yellow at  $173^\circ$ , melting at  $174-176^\circ$  to a brown liquid. The dried salt dissolves readily in absolute methyl or ethyl alcohol, separating from the latter on rubbing, presumably with alcohol of crystallization.

*Analyses.* Calc. for  $(C_{20}H_{23}O_2N_2)_2 \cdot H_2SO_4 \cdot 3H_2O$ :  $H_2O$ , 6.72. Found: 6.67. Calc. for  $(C_{20}H_{23}O_2N_2)_2 \cdot H_2SO_4$ : N, 7.47;  $SO_4$ , 12.79. Found: N, 7.47,  $SO_4$ , 12.68.

**N-Methylquinicine Dihydrochloride.**—Quinidine methiodide was decomposed according to the method Freund and Rosenstein<sup>10</sup> used in the case of cinchonine methiodide, namely, heating in an autoclave with an excess of strong alkali. According to the literature the salts are oily, but a test portion eventually crystallized when treated with an excess of conc. hydrochloric acid, diluted with dry acetone, and allowed to evaporate spontaneously, with replacement of the acetone from time to time and rubbing. The base was accordingly dissolved in a little absolute alcohol, acidified to wet congo red paper with conc. hydrochloric acid, diluted with dry acetone until the initial turbidity just redissolved, and seeded. Crystallization of the salt as rhombic aggregates was completed by rubbing and adding more dry acetone from time to time. The dihydrochloride was recrystallized by a similar process. The air-dry salt dissolves readily in water with a bright yellow color, appearing greenish in thin layers and turning more greenish on dilution. It has a definite anesthetic effect on the tip of the tongue. Dried *in vacuo* at room temperature over sulfuric acid it gives  $[\alpha]_D^{23} +16.6^\circ$  in water,  $c=0.992$ , and softens at  $140-150^\circ$  to a jelly, melting at  $153-155^\circ$  to give a yellow liquid containing bubbles. The substance gives the thalleoquinine test. The base obtained from the purified salt did not crystallize.

*Analyses.* Calc. for  $C_{21}H_{25}O_2N_2 \cdot 2HCl \cdot H_2O$ :  $H_2O$ , 4.20. Found: 4.63. Calc. for  $C_{21}H_{25}O_2N_2 \cdot 2HCl$ : N, 6.82; Cl, 17.24. Found: N, 6.91; Cl, 16.89.

**N-Methyl-dihydroquinicine Hydrochloride.**—Sixty g. of dihydroquinine methiodide were heated for 4 hours at  $160-165^\circ$  in an autoclave with 300 cc. of water and 22 g. of sodium hydroxide.<sup>10</sup> The oil obtained from the ether extract was taken up in absolute alcohol. After neutralizing with absolute alcoholic hydrochloric acid the solution was concentrated *in vacuo*, dissolved in the minimum amount of dry acetone, and seeded with crystals obtained from a similarly treated test portion. Concentration of the mother liquor and addition of ether yielded a second crop, a total of 25 g. being obtained. Recrystallized from absolute alcohol by the addition of dry ether, the hydrochloride separates as cream colored microscopic prisms and needles with wedge-shaped ends. It dissolves in water to form a solution with a dull yellow color, which changes to the characteristic bright yellow-green of the quinicine di-acid salts on adding dil. hydrochloric acid. An aqueous solution has a slowly developing, definite anesthetic effect on the tip of the tongue. The air-dry salt softens to a jelly at about  $120^\circ$  and melts completely at about  $145^\circ$ . The anhydrous compound, when rapidly heated to  $150^\circ$ , then slowly, melts to a jelly at  $150-153^\circ$  and is completely fluid at  $163^\circ$ . It dissolves readily in absolute alcohol, dry acetone, or chloroform, and gives  $[\alpha]_D^{26.5} -9.4^\circ$  in water;  $c=1.015$ .

*Analyses.* Calc. for  $C_{21}H_{25}O_2N_2 \cdot HCl \cdot 0.5H_2O$ :  $H_2O$ , 2.34. Found: 2.93. Calc. for  $C_{21}H_{25}O_2N_2 \cdot HCl$ : N, 7.44; Cl, 9.41. Found: N, 7.46; Cl, 9.27.

The base obtained from the purified salt failed to crystallize.

**N-Ethyl-quinicine Hydrochloride.**—The oily base obtained from quinidine ethyl bromide was converted into the salt as in the preceding cases. Recrystallized twice from 95% alcohol, it separates as faintly yellow, short rods which are anhydrous. It is quite soluble in dry methyl alcohol and slowly but freely soluble in water, the aqueous

<sup>10</sup> Freund and Rosenstein, *Ann.*, 277, 279 (1893).



solution being weakly bitter and having definite anesthetic properties. It gives a dark blue-gray thalleoquinine test, changing to lilac. When rapidly heated to 200°, then slowly, it softens at 201°, and melts at 202–204° to a dark liquid which slowly decomposes.  $[\alpha]_D^{23}$  is +68.1° in water,  $c=0.665$ , a much higher value than that obtained in the case of other closely related salts.

*Analyses.* Calc. for  $C_{22}H_{28}O_2N_2 \cdot HCl$ : N, 7.21; Cl, 9.12. Found: N, 7.33; Cl, 9.02.

**N-Ethyl-dihydroquinicine Hydrochloride.**—This salt, obtained from dihydroquinine ethyl bromide (see below), was recrystallized from absolute alcohol and forms rosetts of minute platelets which, when rapidly heated to 195°, then slowly, soften to a dark tar at 196–198° and melt completely at 202°. It dissolves readily in dry methyl alcohol or chloroform, less readily in absolute alcohol, and sparingly in boiling dry acetone.  $[\alpha]_D^{27}$  is –14.4° in water;  $c=1.007$ . It also has anesthetic properties.

*Analyses.* Calc. for  $C_{22}H_{28}O_2N_2 \cdot HCl$ : N, 7.17; Cl, 9.07. Found: N, 7.88; Cl, 8.98.

**N-Benzyl-dihydroquinicine Hydrochloride.**<sup>11</sup>—The crude base was taken up in dry acetone, neutralized with absolute alcoholic hydrochloric acid, and seeded with crystals obtained by evaporating a neutral alcoholic solution, adding dry acetone, and letting stand. The yield was 10.1 g. Recrystallized from absolute alcohol with the aid of dry ether the salt forms rosetts of long, narrow platelets. It dissolves readily in methyl alcohol or chloroform, less easily in cold absolute alcohol, and turns gummy under a little water, dissolving on dilution without color, and turning pale yellow on adding hydrochloric acid. When rapidly heated to 160°, then slowly, it melts with slight preliminary softening at 161–164°, with slow decomposition.  $[\alpha]_D^{24.6}$  in 50% alcohol is –65.9°;  $c=1.093$ . It also has anesthetic properties.

*Analyses.* Calc. for  $C_{27}H_{32}O_2N_2 \cdot HCl$ : N, 6.19; Cl, 7.83. Found: N, 6.23; Cl, 7.71.

**Ethyl-dihydrocupreicine (Optotoxine) Sulfate.**—Although the quinicine prepared from ethyl-dihydrocupreine (optochin) is mentioned by Morgenroth<sup>12</sup> we have been unable to find any description of the base or its salts. The sulfate was found to crystallize readily, and was prepared as follows: 50 g. of ethyl-dihydrocupreine (Zimmer) were dissolved in 600 cc. of water and 100 cc. of 50% acetic acid and boiled in an oil-bath for 30–35 hours.<sup>13</sup> The free base obtained from the brown-orange solution was taken up in absolute alcohol and made very slightly acid with conc. sulfuric acid. The sulfate separated slowly when left in the cold and after rubbing. The filtrate yielded more when treated with dry acetone and ether. The yield was 28 g. Recrystallized from absolute alcohol it forms voluminous, hair-like needles which dissolve in water to form a solution with a pale greenish-yellow color changing to an intense lemon-yellow with a little mineral acid. The anhydrous salt melts at 164–166° to give a yellow liquid, has  $[\alpha]_D^{28}$  –7.8° in water,  $c=1.090$ , dissolves readily in methyl alcohol, rather sparingly in cold absolute alcohol, and gelatinizes under dry chloroform, dissolving with difficulty. It acts as an anesthetic on the tip of the tongue.

*Analyses.* Calc. for 2.5 H<sub>2</sub>O: 5.47. Calc. for 1 C<sub>21</sub>H<sub>28</sub>OH: 5.59. Found: 5.81. Calc. for (C<sub>21</sub>H<sub>28</sub>O<sub>2</sub>N<sub>2</sub>)<sub>2</sub>·H<sub>2</sub>SO<sub>4</sub>: N, 7.20; SO<sub>4</sub><sup>==</sup>, 12.33. Found: N, 7.41; SO<sub>4</sub><sup>==</sup>, 12.34.

**Dihydrocupreicine Hydrobromide.**—Twenty-five g. of crude, oily dihydroquinicine<sup>14</sup> were demethylated with aqueous hydrobromic acid (sp. gr. 1.49).<sup>15</sup> The solution

<sup>11</sup> THIS JOURNAL, 41, 2102 (1919).

<sup>12</sup> Morgenroth, cf. C. A., 13, 2207 (1919).

<sup>13</sup> Cf. v. Miller and Rohde, Ber., 28, 1064 (1895).

<sup>14</sup> P. 1086.

<sup>15</sup> Cf. THIS JOURNAL, 41, 821 (1919).

was concentrated to dryness *in vacuo*, taken up in a little hot water, cooled, and 10% aqueous sodium hydroxide was cautiously added until considerable precipitate formed but the solution still remained faintly acid to litmus. The collected salt was recrystallized from water, separating as olive-yellow aggregates of pointed platelets. The yield was 12.5 g. The hydrobromide melts slowly, with slight preliminary softening, at 213–215° to a brown liquid which gradually blackens. It dissolves in water to form a solution with a yellow color, which becomes more intense on further addition of acid. A dilute aqueous solution gives a deep olive-brown color with ferric chloride and, when made alkaline, couples readily with diazotized sulfanilic acid. It dissolves with difficulty in cold absolute alcohol, more easily on boiling, and is quite soluble in cold dry methyl alcohol. A concentrated aqueous solution gives an orange colored precipitate of the base with ammonia, but the base could not be made to crystallize.  $[\alpha]_D^{21.6}$  in water is  $-5.4^\circ$ ;  $c=0.827$ .

*Analyses.* Calc. for  $C_{19}H_{24}O_2N_3 \cdot HBr$ : N, 7.13; Br, 20.32. Found: N, 7.31; Br, 20.11.

### B. Glycine Derivatives of Quinicine

**Quinicylglycin-anilide Dihydrochloride**,  $R:N \cdot CH_2CONHC_6H_5, 2HCl$ .—Four g. of quinicine oxalate, 1.7 g. of chloro-acetanilide, 2 g. of sodium iodide, 4 g. of crystalline sodium acetate, 25 cc. of alcohol, 10 cc. of *N* sodium hydroxide solution, and 15 cc. of water were boiled on the water-bath for 3 hours, with a little more alcohol to hold in solution the brown oil which soon began to separate. An additional 10 cc. of *N* sodium hydroxide was finally added and the mixture diluted with hot water, precipitating a greenish gum which resisted all efforts at crystallization. After washing with water it was treated with about 25 cc. of 1:1 hydrochloric acid. The dihydrochloride which crystallized was taken up in hot water, the solution boiled with bone black to remove impurities, and the filtrate chilled and treated with hydrogen chloride until just turbid. The salt separated as sheaves and rosetts of delicate, pale yellow needles. Crystallization was completed by passing in more hydrogen chloride, the total yield being 2.3 g. The substance is rather sparingly soluble in cold water, more easily on warming, with a yellow color, and when dry gradually sinters to a jelly above 130°, melting and evolving gas at about 190°.

*Analyses.* Calc. for  $C_{28}H_{31}O_4N_3 \cdot 2HCl$ : N, 7.93; Cl, 13.37. Found: N, 8.16; Cl, 13.95.

**Quinicylglycine-*p*-hydroxyanilide Acid Sulfate**.—This substance was prepared as in the case of the preceding compound, using *p*-chloro-acetyl-amino-phenol.<sup>15</sup> As neither the base nor the dihydrochloride crystallized, the crude product was rubbed with 25% sulfuric acid, when it soon became crystalline. Recrystallized from 50% alcohol containing a drop of dil. sulfuric acid, it formed rosetts of orange colored leaflets and needles which were dried *in vacuo*. It melts at 212–215° with preliminary darkening and softening, and is very difficultly soluble in cold water but dissolves on boiling. It is also sparingly soluble in absolute alcohol or dry methyl alcohol, and dissolves in dil. sodium hydroxide solution with the formation of a pale yellow color.

*Analyses.* Calc. for  $C_{28}H_{31}O_4N_3 \cdot H_2SO_4$ : N, 7.36;  $SO_4^{=}$ , 16.82. Found: N, 7.28;  $SO_4^{=}$ , 17.12.

### C. Hydrochlorides of Certain Benzoylated Cinchona Alkaloids

**Benzoyl-cinchonidine Dihydrochloride**.—Thirty g. of powdered cinchonidine were added in small portions to 60 g. of benzoyl chloride on the water-bath, with stirring.<sup>17</sup>

<sup>15</sup> THIS JOURNAL, 39, 1442 (1917).

<sup>17</sup> Cf. Wunsch, *Compt. rend.*, 119, 407 (1894).

The salt suddenly separated before all of the alkaloid had gone into solution and heating was continued for 45 minutes. An equal volume of dry acetone was added and the mixture boiled under a reflux condenser until the lumps had hardened, after which they were ground up in a mortar and again boiled for several hours. The yield was 33.8 g. Recrystallized from absolute alcohol by the addition of dry ether, the salt formed rosetts of club-shaped, prismatic needles. The anhydrous salt darkens and sinters above 200°, melting and decomposing at 208–211°; it dissolves readily in water or methyl alcohol, less easily in dry chloroform, and sparingly soluble in cold absolute alcohol but readily on warming.

*Analyses.* Calc. for  $C_{28}H_{30}O_2N_2 \cdot 2HCl \cdot H_2O$ :  $H_2O$ , 3.68. Found: 3.05. Calc. for  $C_{28}H_{30}O_2N_2 \cdot 2HCl$ : N, 5.95; Cl, 15.04. Found: N, 5.99; Cl, 14.77.

**Benzoyl-dihydrocinchonidine Hydrochloride.**—When 19.7 g. of benzoylcinchonidine dihydrochloride were dissolved in 150 cc. of water, treated with 5 cc. of 2% palladium chloride solution, and shaken with hydrogen, the calculated amount of gas was absorbed. The filtered solution was diluted and the base precipitated with ammonia, 15.4 g. of amorphous product being obtained. A solution of the base in absolute alcohol was neutralized with absolute alcoholic hydrochloric acid and treated with dry ether. The salt thus obtained was recrystallized by a similar process and formed rhombic crystals which were air-dried. It is rather sparingly soluble in water, dissolves slowly but freely in absolute alcohol or dry acetone, and is easily soluble in dry chloroform. The anhydrous salt gives  $[\alpha]_D^{27.6} + 124.9^\circ$  in absolute alcohol,  $c = 1.093$ , and softens to a jelly at 160–165°, gradually melting at 185–190° to form a yellow liquid filled with bubbles.

*Analyses.* Calc. for  $C_{28}H_{30}O_2N_2 \cdot HCl \cdot H_2O$ :  $H_2O$ , 3.96. Found: 3.74. Calc. for  $C_{28}H_{30}O_2N_2 \cdot HCl$ : N, 6.42; Cl, 8.12. Found: N, 6.65; Cl, 8.19.

**Benzoylquinine Dihydrochloride.**—Anhydrous quinine when treated 45 minutes with benzoyl chloride yielded a crystalline salt.<sup>17</sup> This was recrystallized as in the preceding case, forming short, transparent prisms which were warmed to 60° for a few moments, evacuated and air-dried. It dissolves readily in water, methyl alcohol or chloroform, and somewhat less easily in absolute alcohol. The anhydrous salt gives  $[\alpha]_D^{22} + 88.7^\circ$  in water,  $c = 0.892$ , and when rapidly heated to 225°, then slowly, turns yellow and softens, finally melting and decomposing at 229–232°.

*Analyses.* Calc. for  $C_{27}H_{30}O_2N_2 \cdot 2HCl \cdot H_2O$ :  $H_2O$ , 3.59. Found: 4.21. Calc. for  $C_{27}H_{30}O_2N_2 \cdot 2HCl$ : N, 5.59; Cl, 14.15. Found: N, 5.95; Cl, 13.96.

**Benzoyl-dihydroquinine Hydrochloride.**—Benzoylquinine dihydrochloride was reduced in the same way as the cinchonidine analog, and the crude, amorphous base was converted into the hydrochloride as in the case of the dihydrocinchonidine analog. The solution was concentrated to dryness *in vacuo* and the residue was dissolved in dry acetone, treated with dry ether, and then with ligroin until slightly turbid. The salt gradually crystallized and was purified by a repetition of the process, separating as flat, cream colored prisms which dissolve sparingly in cold water. The anhydrous salt melts and decomposes at 235–240° with preliminary softening and gives  $[\alpha]_D^{24} + 140.6^\circ$  in absolute alcohol;  $c = 1.298$ .

*Analyses.* Calc. for  $C_{27}H_{30}O_2N_2 \cdot HCl \cdot 0.5H_2O$ :  $H_2O$ , 1.89. Found: 1.92. Calc. for  $C_{27}H_{30}O_2N_2 \cdot HCl$ : N, 6.00; Cl, 7.60. Found: N, 6.10; Cl, 7.55.

## Tenine Ester Derivatives

**Cinchotinine Methyl Ester.**—Anhydrous cinchotinine was esterified in dry methyl alcoholic solution by saturation with dry hydrogen chloride. After removing the alcohol the ester was obtained from an aqueous solution of the residue by cautiously adding

sodium carbonate solution. Recrystallized from alcohol it forms glistening prismatic plates which dissolve rather sparingly in the cold in the usual neutral solvents. When rapidly heated to  $240^{\circ}$ , then slowly, the ester darkens and sinters above this point, melting and decomposing at  $243-244.5^{\circ}$ .  $[\alpha]_D^{22}$  in methyl alcohol is  $+118.7^{\circ}$ ;  $c=0.206$ .

*Analysis.* Calc. for  $C_{15}H_{24}O_2N_2$ : N, 8.59. Found: N, 8.70.

**Cinchotenine Ethyl Ester Hydrochloride.**—This salt was prepared by neutralizing a solution of the ester base in absolute alcohol, and treating with dry ether. The salt separated as aggregates of minute plates which decompose at about  $250^{\circ}$ .

*Analyses.* Calc. for  $C_{20}H_{34}O_2N_2 \cdot HCl \cdot 0.5H_2O$ :  $H_2O$ , 2.34. Found: 2.31. Calc. for  $C_{20}H_{34}O_2N_2 \cdot HCl$ : Cl, 9.41. Found: 9.70.

**Cupretenine (Quitenol)<sup>18</sup> Methyl Ester Dihydrochloride.**—The ester was prepared and isolated as in the case of the cinchotenine analog. The dried, amorphous ester was converted into the dihydrochloride by means of an excess of absolute alcoholic hydrochloric acid and the solution treated with dry ether. Recrystallized in the same way it formed rosetts of silky needles which gradually softened and turned yellow when heated, melting to a paste and evolving gas at about  $200^{\circ}$ . It is readily soluble in methyl alcohol and in water, the aqueous solution coupling with diazotized sulfanilic acid when made alkaline.

*Analyses.* Calc. for  $C_{15}H_{22}O_4N_2 \cdot 2HCl$ : N, 6.51; Cl, 17.07. Found: N, 6.70; Cl, 16.30.

### Crystalline Ethyl-dihydrocupreine (Optochin) and Other Simple Cinchona Derivatives

**Ethyl-dihydrocupreine (Optochin).**—Led by the ease with which we found dihydroquinine to crystallize from toluene we attempted to obtain ethyl-dihydrocupreine crystals from this solvent. The base dissolved easily, and on allowing the solution to evaporate spontaneously, crystals soon formed on the walls of the vessel. Five g. of the amorphous base (Zimmer) were accordingly dissolved in about 10 cc. of hot toluene, cooled, and seeded, the base gradually crystallizing as aggregates of irregular platelets which were again recrystallized from toluene, additional amounts being obtained from the mother liquors on adding ligroin and seeding. The crystals retained toluene of crystallization even on air drying, but as the combustions obtained on such products indicated that water was present as well, we are unable to say how much toluene was retained. The air-dry substance gives  $[\alpha]_D^{26.6} - 112.7^{\circ}$  in absolute alcohol,  $c=1.002$ , melts at  $80-4^{\circ}$  with preliminary softening, and is less soluble in benzene, toluene, or ligroin than in the other usual organic solvents. After removing the toluene and water *in vacuo* first at room temperature, then at  $100^{\circ}$ , the residue melted at  $123-128^{\circ}$  with preliminary softening and gave  $[\alpha]_D^{25} - 136.2^{\circ}$  in absolute alcohol,  $c=1.005$ , figures comparable with those given by the best commercial specimens of the amorphous base.

*Analyses.* Subs., air-dry, 0.3254: loss, 0.0510, or 15.87%; 15.66 on another preparation. Calc. for  $C_{21}H_{32}O_2N_2$ : C, 74.07; H, 8.29. Found: C, 74.31; H, 8.17.

**Ethyl-dihydrocupreine Ethyl Bromide.**—Two g. of the base and a slight excess of ethyl bromide were boiled in dry acetone for 4 hours, and the solvent then boiled off. The residue gradually crystallized on standing, as a radiating fibrous mass. This was recrystallized by dissolving in boiling dry acetone and adding dry ether. After further recrystallization it forms rosetts of minute, rhombic plates which dissolve quite readily in water, especially on warming. The anhydrous bromide gives  $[\alpha]_D^{25} - 111.8^{\circ}$  in water,  $c=1.100$ , softens to a viscous mass above  $120^{\circ}$  and at  $185^{\circ}$  yields a completely fluid,

<sup>18</sup> Quitenine was demethylated by boiling with hydrobromic acid (sp. gr. 1.49) instead of with hydriodic acid, as given by Bucher, *Monatsh.*, 14, 603 (1893).

yellow mass containing bubbles. It dissolves readily in methyl or ethyl alcohol, acetone, or chloroform.

*Analyses.* Calc. for  $C_{22}H_{33}O_2N_2Br \cdot H_2O$ :  $H_2O$ , 3.86. Found: 3.89. Calc. for  $C_{22}H_{33}O_2N_2Br$ : Br, 17.78. Found: 17.72.

**Dihydroquinine Ethyl Bromide.**—The components were boiled for 4 hours in a mixture of equal volumes of dry chloroform and dry acetone. Washed with acetone and recrystallized first from water and then from alcohol by adding ether, the salt formed rosetts of glistening platelets. When anhydrous it gives  $[\alpha]_D^{22.5} -111.1^\circ$  in water  $c=1.004$ , and when rapidly heated to  $185^\circ$ , then slowly, melts slowly at  $188-190^\circ$  with slight decomposition. It is less soluble in acetone than the optochin derivative.

*Analyses.* Calc. for  $C_{22}H_{31}O_2N_2Br \cdot 0.5H_2O$ :  $H_2O$ , 2.03. Found: 2.06. Calc. for  $C_{22}H_{31}O_2N_2Br$ : Br, 18.36. Found: 18.31.

**Hydrobromocinchonidine.**—This substance was prepared as in the case of the hydrobromo compound described in the next paragraph, and to Leger's<sup>19</sup> description we can add only the following data. When rapidly heated to  $175^\circ$ , then slowly, the base discolors somewhat and melts to form a reddish liquid, with decomposition, at  $176-177^\circ$ .  $[\alpha]_D^{21.5}$  is  $-226.8^\circ$  in dry methyl alcohol;  $c=0.1608$ .

*Analysis.* Calc. for  $C_{19}H_{21}ON_2Br$ : N, 7.47. Found: N, 7.52.

**Hydrobromocupreine (or hydrobromo-apoquinine)dihydrobromide.**—Ten and a half g. of quinine were heated for 6 hours at  $110^\circ$  in an oil-bath with 60 cc. of hydrobromic acid (sp. gr. 1.49). On cooling and standing for several days the above salt crystallized. Recrystallized from water containing a little hydrobromic acid, the dihydrobromide separated as delicate, tawny, voluminous needles. The yield was 4.5 g. Like solutions of the di-acid dihydrocupreine salts, the very faintly yellow solution in water turns a deeper yellow on neutralization (the reverse of the phenomena observed in the case of the quinicines), and then gives a pale brown color with ferric chloride. The base is precipitated by sodium carbonate, redissolving on adding sodium hydroxide to yield a solution which couples with diazotized sulfanilic acid. The anhydrous salt gives  $[\alpha]_D^{21} -161.8^\circ$  in water,  $c=1.022$ , and softens slightly when heated, sintering at  $190-195^\circ$  and slowly intumescing at  $197-203^\circ$ . It is somewhat soluble in cold absolute alcohol, the solution crystallizing on rubbing.

*Analyses.* Calc. for  $C_{19}H_{21}O_2N_2Br \cdot 2HBr \cdot 3.5H_2O$ :  $H_2O$ , 10.23. Found: 10.24. Calc. for  $C_{19}H_{21}O_2N_2Br \cdot 2HBr$ : Br<sup>-</sup>, 28.91. Found: 29.20.

[CONTRIBUTION FROM THE LABORATORIES OF THE ROCKEFELLER INSTITUTE FOR MEDICAL RESEARCH]

## SYNTHESES IN THE CINCHONA SERIES. X. DIHYDROCINCHONICINOL AND THE DIHYDROQUINICINOLS<sup>1</sup>

BY MICHAEL HEIDELBERGER AND WALTER A. JACOBS

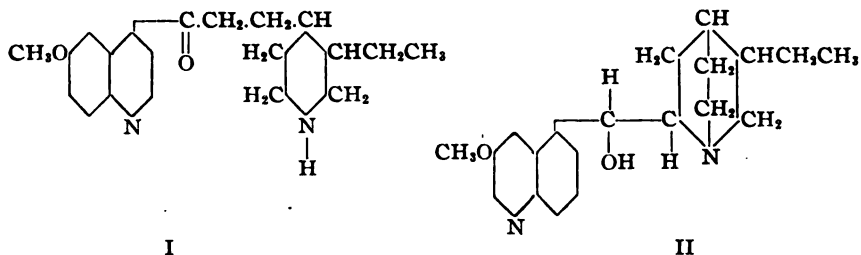
Received July 28, 1921

In the course of the bacteriological study of certain cinchona derivatives undertaken in conjunction with Dr. Martha Wollstein and Dr. Lloyd D. Felton it developed that in general the dihydrogenated alkaloids of the quinicine type (I) were less pneumococcidal than the original alkaloids (II) from which they were derived. While it seemed possible

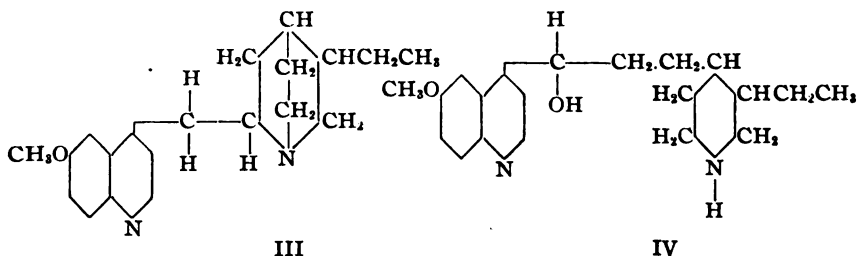
<sup>19</sup> Leger, *Bull. soc. chim.*, [4] 25, 572 (1919).

<sup>1</sup> Presented at the Annual Meeting of the American Chemical Society, New York, September, 1921.

that this effect was in some way due to the breaking up of the fused quinclidene nucleus into the simpler piperidine ring, it seemed also possible that the loss of the secondary hydroxyl group might play a part, especially



as dihydroquinane and its related alkaloids,<sup>2</sup> (III) in which the quinclidene nucleus is still intact, had previously been found to be less active than the parent alkaloids. It was therefore hoped that the restoration of the secondary alcohol group in the quinicine series would enhance the pneumococcidal power of these alkaloids. While it was found possible to reduce the keto group in the desired sense, the resulting alkaloids (IV) were devoid of marked pneumococcidal power, even when the tertiary character of the piperidine nitrogen atom was restored by methylation or ethylation.

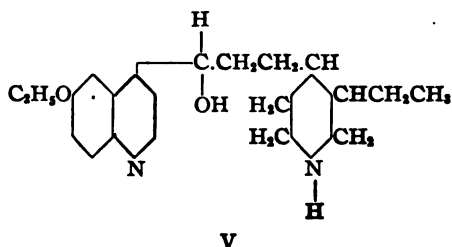


The reduction was accomplished with the aid of palladium black and hydrogen, and we have named the new alkaloids so prepared the dihydrocinchoncinols and dihydroquinicinols, depending on whether the alkoxy group is absent or present. It is obvious that in the reduction of the keto group the central carbon atom is restored to its original condition of asymmetry, so that optical isomers should result. The reduction products proved, as expected, to be mixtures and, depending on the particular case, could be separated into the optical isomers either as the free base or as an appropriate salt. In every case the *d*-compound proved the easier to isolate, and of those investigated, only in the case of *N*-methyl-dihydroquinicinol, could both the *d*- and *l*-bases be obtained crystalline. Dihydrocinchoncinol was separated into the *d*- and *l*-sulfates; *d*-dihydroquinicinol crystallized, but the *l*-isomer could be isolated only as the

<sup>2</sup> THIS JOURNAL, 42, 1489 (1920).

dihydrochloride; *d*-N-ethyl-dihydroquinicinol and *d*-O-ethyl-dihydrocupreicinol (V) (corresponding to ethyldihydrocupreine, or optochin), were obtained crystalline, and while in the former case a second dihydrochloride was obtained, no crystalline derivative of *l*-O-ethyl-dihydrocupreicine could be prepared. The mixture of N-benzyl-dihydroquinicins also failed to yield crystalline derivatives.

*d*-N-Methyl-dihydroquinicinol and *d*-N-ethyl-dihydroquinicinol were also prepared by alkylation of the parent *d*-dihydroquinicinol, and similar derivatives were also formed from *d*-O-ethyl-dihydrocupreicinol, crystallizing with little difficulty.



An interesting consequence of the restoration of the secondary hydroxyl group in the case of the dihydroquinicins (and O-ethyl-dihydrocupreicinol) was the restoration of the bluish fluorescence of the bases when dissolved in excess nitric or sulfuric acid, thus supporting Kaufmann's statement that the alkoxy group and the secondary hydroxyl are necessary to produce this phenomenon.<sup>3</sup> The dilute acid solutions were also relatively stable to potassium permanganate.

It is hoped soon to study the pharmacological properties of this new series of alkaloids.

### Experimental

*d*- and *l*-Dihydrocinchoncinol Sulfates.<sup>4</sup>—Fifty g. of air-dry cinchonine oxalate were dissolved in water and dil. hydrochloric acid, the solution made alkaline with sodium hydroxide, shaken out with ether, and the extract dried for a few moments and concentrated. The residue was taken up in about 100 cc. of water and 14 g. of conc. sulfuric acid and shaken in an atmosphere of hydrogen with the palladium black from 8 cc. of 2% palladium chloride solution, with the addition of 3 cc. of the palladium chloride solution after reduction had commenced, in order to accelerate the reaction. The absorption was 5570 cc. (Calc. for 2H<sub>2</sub>, 5965 cc.). In a later experiment cinchonine oxalate itself was reduced after dissolving with the aid of an equivalent of sulfuric acid and the absorption found to be slightly greater than that calculated. The solution was diluted, decanted from the palladium, made alkaline with sodium hydroxide, and the base extracted with ether. The ether extract was thoroughly dried, finally over sodium

<sup>3</sup> Kaufmann, *Ber.*, 46, 1827 (1913).

<sup>4</sup> After most of the work on the quinicins had been completed it was found that Kaufmann and Huber [*Ber.*, 46, 2919 (1913)] mention that cinchonine absorbs 4 atoms of hydrogen, giving yellowish, oily "hydrocinchotoxol" which was not investigated.

hydroxide, concentrated, dissolved in 150 cc. of absolute alcohol and made just barely acid to litmus with conc. sulfuric acid. On seeding with crystals obtained from a portion which was precipitated with dry acetone and allowed to stand for several days, 7.6 g. of the crude *d*-sulfate gradually crystallized. This was recrystallized first from absolute alcohol, then boiled out with a little absolute alcohol, and finally dissolved in the minimum amount of 95% alcohol. Dry acetone was then added to marked turbidity, followed by treatment with bone black and filtering, and again the addition of dry acetone to incipient turbidity. The rotation of the salt which then crystallized was found to have attained a constant value.

*d*-Dihydrocinchoninic sulfate forms cream colored, microscopic needles which dissolve readily in water to form a solution with a pale yellow color and are difficultly soluble in absolute alcohol, but somewhat more so in dry methyl alcohol. The anhydrous salt sinters and turns brown at 222°, melting at 223–224° with slow gas evolution, and gives  $[\alpha]_D^{20} + 63.6^\circ$  in water;  $c = 1.014$ .

*Analyses.* Calc. for  $(C_{19}H_{21}ON_2)_2 \cdot H_2SO_4 \cdot 2H_2O$ : H<sub>2</sub>O, 4.93. Found: 5.23. Calc. for  $(C_{19}H_{21}ON_2)_2 \cdot H_2SO_4$ : C, 65.65; H, 7.84; N, 8.07; SO<sub>4</sub><sup>−</sup>, 13.83. Found: C, 65.35; H, 7.47; N, 8.27; SO<sub>4</sub><sup>−</sup>, 13.98.

The filtrate from the crude *d*-sulfate was treated with dry acetone and stirred until the initial gummy precipitate dissolved with difficulty, the solution bottled, and allowed to stand in the ice-box for about 2 weeks. The drab-colored precipitate, which resembled the first fraction, weighed 9.1 g., but after recrystallization from absolute alcohol only 2.2 g. were recovered, and the product was strongly levorotatory. It was accordingly boiled with a little absolute alcohol, cooled, the colored alcoholic solution poured off, and the residue dissolved in boiling dry methyl alcohol. Dry acetone was then added to incipient turbidity, the solution treated with bone black and rapidly filtered; more dry acetone was added to incipient turbidity and the mixture allowed to stand. The *l*-sulfate separated as rosetts of minute, cream colored leaflets which were dried *in vacuo* over sulfuric acid.  $[\alpha]_D^{32}$  in water was constant at  $-57.3^\circ$ ;  $c = 1.109$ . When rapidly heated to 230°, then slowly, the salt melts with preliminary softening at 232–234°, with gas evolution. In properties, as well as in appearance, it greatly resembles its optical isomer.

*Analyses.* Calc. for  $(C_{19}H_{21}ON_2)_2 \cdot H_2SO_4$ : C, 65.65; H, 7.84; N, 8.07; SO<sub>4</sub><sup>−</sup>, 13.83. Found: C, 65.74; H, 7.87; N, 8.14; SO<sub>4</sub><sup>−</sup>, 14.03.

Neither the *d*- nor *l*-base, liberated from its sulfate, could be made to crystallize.

On addition of more dry acetone to the mother liquors from the *d*- and *l*-sulfates mixtures of the *d*- and *l*-forms were obtained.

#### Dihydroquinicinal

*d*-Dihydroquinicinal Nitrate.—Sixty g. of recrystallized quinine hydrochloride<sup>a</sup> were dissolved in 180 cc. of water and 7.5 cc. of conc. sulfuric acid and reduced with palladium and hydrogen. The absorption was 7655 cc. (Calc. for 2 H<sub>2</sub>, 7453 cc.) The filtrate from the palladium was neutralized to litmus with 10% aqueous sodium hydroxide, and care was taken to redissolve the gummy precipitate locally formed by the alkali. To the filtered solution (about 350 cc.), powdered sodium nitrate was added to incipient turbidity and the mixture allowed to stand for several days, with occasional rubbing. The crystalline deposit weighed 28 g. after washing with 5% sodium nitrate solution. Recrystallized first from 25% alcohol, then from absolute alcohol, the nitrate forms faintly yellow rhombs which yield a white powder when ground. It is sparingly soluble in cold water, quite readily on boiling, the solution giving a blue-violet fluorescence with a little nitric or sulfuric acid and also giving the thalleoquinine test.

<sup>a</sup> THIS JOURNAL, 41, 832 (1919).



When rapidly heated, the air-dry salt melts at 125–135° with effervescence and preliminary softening, but when anhydrous it softens above 90°, begins to melt at 95°, and is completely fluid at 115°.  $[\alpha]_D^{27.5}$  of the anhydrous salt is +100.7° in 50% alcohol;  $c = 1.063$ .

*Analyses.* Calc. for  $C_{20}H_{28}O_2N_2 \cdot HNO_3 \cdot H_2O$ :  $H_2O$ , 4.40; C, 58.64; H, 7.64. Found:  $H_2O$ , 4.35; C, 58.73; H, 7.68.<sup>6</sup> Calc. for  $C_{20}H_{28}O_2N_2 \cdot HNO_3$ : N, 10.74. Found: 10.92.

*d*-Dihydroquinicinal.—The purified nitrate was converted into the base with alkali and shaken out with ether. After removing the solvent the warm residue was dissolved in a little hot benzene, with which it is miscible only if too much is not used. After cooling to room temperature and seeding with crystals obtained by allowing a test portion in benzene to evaporate spontaneously, the base crystallized rapidly as cream colored rhombs which were washed with a little cold benzene and air dried. It dissolves readily in alcohol, acetone or chloroform and turns gummy under dry ether or toluene, then dissolving with difficulty. It begins to sinter at 68° and is completely fluid at about 80°.  $[\alpha]_D^{26}$  of the anhydrous base is +87.1° in absolute alcohol;  $c = 1.045$ .

*Analyses.* Calc. for  $C_{20}H_{28}O_2N_2 \cdot 0.5H_2O$ :  $H_2O$ , 2.66. Found: 2.34. Calc. for  $C_{20}H_{28}O_2N_2$ : C, 73.12; H, 8.60; N, 8.53. Found: C, 73.39; H, 8.63; N, 8.33.

*d*-Dihydroquinicinal Dihydrochloride.—An absolute alcoholic solution of the base was acidified to congo red with absolute alcoholic hydrochloric acid. The dihydrochloride gradually separated as rosets of minute needles which dissolve readily in water and rather sparingly in cold absolute alcohol, more easily on boiling. When rapidly heated to 210°, then slowly, the salt melts at 212–214° with gas evolution to form a yellow liquid.  $[\alpha]_D^{31}$  is +151.8° in water;  $c = 1.096$ .

*Analysis.* Calc. for  $C_{20}H_{28}O_2N_2 \cdot 2HCl$ : Cl, 17.67. Found: Cl, 17.54.

*l*-Dihydroquinicinal Dihydrochloride.—In preliminary reduction experiments it was found that on taking up the crude base in absolute alcoholic hydrochloric acid an apparently homogeneous salt crystallized which, on recrystallization from absolute alcohol containing a little hydrochloric acid, finally attained a constant rotation of about +8°. Indeed it was from this salt that it was first found possible to obtain a portion as the *d*-nitrate, thus pointing to the initial isolation of this salt as the best method of separating the optical isomers. On adding more solid sodium nitrate to the filtrate from the first crop of the nitrate until turbid it is not always possible to obtain more of the nitrate free from an oily salt (probably the *l*-nitrate), but unless a considerable amount of the oil is precipitated with the remaining portions of the *d*-nitrate, some of the latter remains in solution, and on subsequent conversion of the filtrate into the dihydrochloride it is impossible to attain maximal levorotation. Accordingly solid sodium nitrate was added to the filtrate from the first crop until considerable oily material separated, and after standing overnight the mixture was treated with bone black, filtered, and the dry base obtained from the filtrate in the usual manner. On dissolving in absolute alcohol containing an excess of dry hydrogen chloride and letting the mixture stand, the *l*-dihydrochloride separated on cooling as rosets of diamond-shaped, glistening platelets which then were repeatedly crystallized from absolute alcohol containing a little absolute alcoholic hydrochloric acid. In this way a maximum  $[\alpha]_D$  of –117.7° was finally obtained in water;  $c = 0.994$ . The salt is very hygroscopic in warm, moist air, and must therefore be filtered in a cold room. It is very soluble in water and rather difficultly so in absolute alcohol, especially in the presence of dry hydrogen chloride. Like the *d*-form it gives the thalleoquinine reaction and fluoresces on adding a suitable acid. The free base was not obtained crystalline. The salt slowly sinters together above 135° and effervesces at 170°.

<sup>6</sup> This analysis refers to a portion recrystallized again from 25% alcohol.

*Analyses.* Calc. for  $C_{30}H_{28}O_2N_2 \cdot 2HCl$ : C, 59.86; H, 7.49; N, 6.98. Found: C, 59.22; H, 7.87; N, 7.67.

Essentially the same results were obtained when dihydroquinicine sulfate<sup>7</sup> was used as the starting material, except that in this case only one molecular equivalent of hydrogen was absorbed.

#### N-Methyl-dihydroquinicinol

*d*-N-Methyl-dihydroquinicinol.—The crude quinicine base from 113.6 g. of quinidine methiodide<sup>8</sup> was dissolved in 300 cc. of 10% sulfuric acid and reduced with 35 cc. of 2% palladium chloride solution and hydrogen. Approximately 2 molecular equivalents of hydrogen were absorbed. The clear centrifuged liquid and washings were diluted, covered with ether, and made alkaline. The residue from the dried ethereal extract crystallized on cooling, and was recrystallized from 50% alcohol, yielding 33 g. of crude *d*-N-methyl-dihydroquinicinol, or almost as much as if the intermediate quiniçine salt<sup>8</sup> had actually been isolated. After 4 recrystallizations from 70% alcohol  $[\alpha]_D^{27}$  was constant at +93.9° in absolute alcohol,  $c=1.012$ , the yield being 8.3 g. The base forms rhombic crystals which are anhydrous and melt at 165.5–166.0° with slight preliminary softening. It is very readily soluble in chloroform, easily in dry methyl or ethyl alcohol, and sparingly in cold dry acetone or benzene but quite soluble on boiling. Dissolved in conc. sulfuric acid it gives a faint yellow color which deepens and shows a green fluorescence when the solution is warmed on the water-bath. It gives the thalleoquinine test and exhibits a violet-blue fluorescence when dissolved in dil. nitric or sulfuric acid.

*Analyses.* Calc. for  $C_{21}H_{20}O_2N_2$ : C, 73.63; H, 8.84; N, 8.19. Found: C, 73.47; H, 8.79; N, 8.34.

*d*-N-Methyl-dihydroquinicinol from *d*-Dihydroquinicinol Nitrate.—A dry acetone solution of *d*-dihydroquinicinol obtained from the nitrate was treated with a slight excess of methyl iodide. Heat was evolved, and when the solution was rubbed the N-methyl hydriodide separated as microscopic rhombs. The collected salt was dissolved in hot water, the solution cooled and treated with an excess of sodium carbonate. The base separated as an oil which soon crystallized on rubbing. After 3 recrystallizations from 70% alcohol  $[\alpha]_D^{30}$  was +93.8° in absolute alcohol,  $c=1.002$ , the melting point 165.5–166.0°, and the other properties also were identical with those of the base obtained from N-methyl-dihydroquinicine.

*d*-N-Methyl-dihydroquinicinol Hydrobromide.—A solution of the base in a slight excess of 10% aqueous hydrobromic acid was neutralized to litmus and the filtrate treated with solid sodium bromide until just turbid. The hydrobromide separated on chilling the solution and letting it stand. Recrystallized from water, it formed a hard crust of rhombs which were anhydrous, and turned pink and softened on heating, melting at 218–223° with darkening. It is rather sparingly soluble in cold water or absolute alcohol, but dissolves readily on heating. With a little sodium iodide or nitrate the aqueous solution soon deposits minute rosetts of the iodide or rhombs of the nitrate.  $[\alpha]_D^{24}$  is +80.2° in water;  $c=1.090$ .

*Analyses.* Calc. for  $C_{21}H_{20}O_2N_2 \cdot HBr$ : N, 6.62; Br, 18.88. Found: N, 7.01; Br, 18.95.

*d*-N-Methyl-dihydroquinicinol Dihydrochloride.—This was obtained as in the case of *d*-dihydroquinicinol dihydrochloride. Recrystallized from absolute alcohol with the aid of dry ether it forms rosetts of glistening platelets, which are extremely easily soluble in water, readily so in absolute alcohol, and practically insoluble in dry

<sup>7</sup> See preceding paper, *THIS JOURNAL*, 44, 1092 (1922).

<sup>8</sup> Ref. 7, p. 1091.

acetone. The salt softens markedly above  $140^{\circ}$ , gradually melting and evolving gas, and becoming completely fluid at about  $190^{\circ}$ .  $[\alpha]_D^{24}$  is  $+145.7^{\circ}$  in water;  $c=1.078$ .

*Analyses.* Calc. for  $C_{21}H_{30}O_2N_2 \cdot 2HCl$ : N, 6.75; Cl, 17.08. Found: N, 6.91; Cl, 16.97.

***d*-N-Methyl-dihydroquinicinicol Methiodide.**—The oily salt separated from a solution of equimolecular parts of the constituents in chloroform, and soon crystallized. After washing with dry acetone it was recrystallized from water, by seeding the solution while still warm and letting it stand in a warm place until crystallization was almost complete, in order to avoid deposition of a gelatinous form. It forms a crust of faintly yellow rhombs which are very difficultly soluble in cold water or absolute alcohol, but more easily on boiling. When rapidly heated to  $220^{\circ}$ , then slowly, it begins to soften above this point and melts at  $225-227^{\circ}$  to a brown, turbid liquid which clears at  $228^{\circ}$ .  $[\alpha]_D^{23.5}$  is  $+68.7^{\circ}$  in water;  $c=1.025$ .

*Analysis.* Calc. for  $C_{21}H_{30}O_2N_2I$ : I, 26.21. Found: 26.27.

***l*-N-Methyl-dihydroquinicinicol.**—The mother liquors from the first two recrystallizations of the crude *N*-methyl dihydroquinicinicol were diluted to incipient turbidity and allowed to stand, when they deposited 8.4 g. of the crude *l*-compound with  $[\alpha]_D -15^{\circ}$  in absolute alcohol. After 2 recrystallizations from 60% alcohol 4.2 g. were obtained with  $[\alpha]_D^{26.5} -24.9^{\circ}$  in absolute alcohol,  $c=1.003$ , the rotation being unchanged by further recrystallization. The *l*-base forms crusts of minute plates which melt with slight preliminary softening at  $136.5-137.5^{\circ}$  to a liquid containing crystals, but becoming clear at  $144^{\circ}$ . It is more soluble in the usual organic solvents than the *d*-isomer, but otherwise greatly resembles this substance.

*Analyses.* Calc. for  $C_{21}H_{30}O_2N_2$ : C, 73.63; H, 8.84; N, 8.19. Found: C, 73.78; H, 8.50; N, 8.04.

The mother liquor from which the first crop of crude *l*-base was obtained still contained considerable amounts of base, which investigation showed to be a mixture.

***l*-N-Methyl-dihydroquinicinicol Dihydrochloride.**—This salt was obtained as in previous cases. Recrystallized from absolute alcohol, with the addition of a drop of absolute alcoholic hydrochloric acid after cooling, it separated as microscopic platelets. It is extremely easily soluble in water, readily so in dry methyl alcohol, sparingly soluble in cold absolute alcohol, and practically insoluble in dry acetone or chloroform. When rapidly heated to  $230^{\circ}$ , then slowly, it decomposes at  $232-235^{\circ}$ . The salt thus melts higher and is less soluble in absolute alcohol than the *d*-isomer.  $[\alpha]_D^{24}$  is  $+1.45^{\circ}$  in water;  $c=1.034$ .

*Analyses.* Calc. for  $C_{21}H_{30}O_2N_2 \cdot 2HCl$ : N, 6.75; Cl, 17.08. Found: N, 7.10; Cl, 17.06.

***l*-N-Methyl-dihydroquinicinicol Methiodide.**—The salt separated from a chloroform solution of the components. Recrystallized from water, it formed cream colored rosetts of thick plates which are sparingly soluble in cold water, readily so in hot, and dissolve very difficultly in boiling absolute alcohol or dry chloroform or acetone. The iodide melts with preliminary browning and softening at about  $253-254^{\circ}$ , with decomposition.  $[\alpha]_D^{23}$  is  $-50.0^{\circ}$  in 50% alcohol;  $c=1.130$ .

*Analysis.* Calc. for  $C_{21}H_{30}O_2N_2I$ : I, 26.21. Found: 26.42.

#### N-Ethyl-dihydroquinicinicol

***d*-N-Ethyl-dihydroquinicinicol.**—The crude quinicine from 93.5 g. of quinidine ethyl bromide<sup>9</sup> was reduced as in the case of the *N*-methyl compound. The crude base

<sup>9</sup> THIS JOURNAL, 44, 1091 (1922).

obtained from the ether extract was taken up in benzene and seeded with crystals obtained on concentration of a test portion of the crude base in ether. The *d*-base gradually crystallized, 12.8 g. being obtained after washing with a little benzene. Recrystallized twice from 70% alcohol it formed colorless, glistening rhombs which melted constantly at 140–141° and gave a constant  $[\alpha]_D^{23}$  of +91.7° in absolute alcohol;  $c=1.030$ . It is readily soluble in the cold in alcohol, methyl alcohol or chloroform, rather sparingly so in cold dry acetone, and difficultly soluble in cold benzene, but readily on boiling. In its reactions it greatly resembles the *N*-methyl derivative.

*Analyses.* Calc. for  $C_{22}H_{25}O_2N_2$ : C, 74.10; H, 9.05; N, 7.86. Found: C, 74.20; H, 8.88; N, 8.26.

*d*-*N*-Ethyl-dihydroquinicinal from *d*-Dihydroquinicinal Nitrate.—The base obtained from the nitrate was treated in acetone solution with 1.2 mols. of ethyl iodide. After several hours the hydriodide separated on rubbing as minute rosetts, and was converted into the base. After 2 crystallizations from 70% alcohol this melted at 140–141° and had attained the maximum  $[\alpha]_D^{26}$  of 92.0° in absolute alcohol;  $c=1.120$ . In analysis and in its properties it also corresponded with the base as obtained directly.

*d*-*N*-Ethyl-dihydroquinicinal Hydrochloride.—Prepared as usual in absolute alcoholic solution the salt deposited after the addition of dry ether. Recrystallized from dry methyl ethyl ketone it formed minute rhombs which are very easily soluble in water. The solution has an intensely bitter taste. The salt dissolves readily in absolute alcohol, less easily in dry acetone, and sparingly in dry chloroform. When anhydrous, it softens at 130° and melts completely at 135° with slight decomposition.  $[\alpha]_D^{20.5}$  in water is +85.4°;  $c=1.043$ .

*Analyses.* Calc. for  $C_{22}H_{25}O_2N_2.HCl.H_2O$ :  $H_2O$ , 4.39. Found: 3.63. Calc. for  $C_{22}H_{25}O_2N_2.HCl$ : N, 7.13; Cl, 9.03. Found: N, 7.55; Cl, 8.97.

*d*-*N*-Ethyl-dihydroquinicinal Dihydrochloride.—The salt was obtained from absolute alcoholic hydrochloric acid with the aid of dry ether and was crystallized by a repetition of the process as minute platelets which are extremely soluble in water, readily in absolute alcohol, and sparingly so in dry acetone or chloroform;  $[\alpha]_D^{23}$  is +142.6° in water;  $c=1.002$ . It softens at about 150° and becomes semifluid, with the formation of gas bubbles at about 180° if slowly heated further, but if rapidly heated it melts and decomposes at about 250°.

*Analysis.* Calc. for  $C_{22}H_{25}O_2N_2.2HCl$ : N, 6.53; Cl, 16.52. Found: N, 6.79; Cl, 16.47.

A portion of the base recovered from the recrystallized salt had not increased in rotation.

*d*-*N*-Ethyl-dihydroquinicinal Methiodide.—A chloroform solution of the components was evaporated to dryness after one-half hour. The addition of dry acetone caused rapid crystallization. When recrystallized from water, the salt separated, oily at first if allowed to cool too quickly, but formed glistening platelets when the solution was seeded while still warm with crystals of the hydrate. When anhydrous it softens above 80°, melting completely at about 135°;  $[\alpha]_D^{21}$  is +62.9° in 50% alcohol;  $c=0.962$ . It also dissolves readily in absolute alcohol or dry chloroform.

*Analyses.* Calc. for  $C_{22}H_{25}O_2N_2.I.2H_2O$ :  $H_2O$ , 6.74. Found: 6.31. Calc. for  $C_{22}H_{25}O_2N_2.I$ : I, 25.48. Found: 25.90.

*l*-*N*-Ethyl-dihydroquinicinal Dihydrochloride.—In a preliminary experiment in which *N*-ethyl dihydroquinicine hydrochloride<sup>10</sup> was used as starting material, the crude base was taken up in hot ligroin and the *d*-base allowed to separate from the warm solvent, cooling resulting in contamination with an oily fraction. The base recovered

<sup>10</sup> THIS JOURNAL, 44, 1094 (1922).

from the ligroin solution was converted as usual into the dihydrochloride. This was recrystallized from absolute alcohol with the aid of a little dry hydrogen chloride and dry ether, forming slightly brownish rosetts which gave  $[\alpha]_D^{25} -16.7^\circ$  in water;  $c=1.081$ . When rapidly heated to  $235^\circ$ , then slowly, it decomposes at  $237-238^\circ$ . The amount obtained was insufficient for recrystallization to constant rotation. A portion, reconverted into the base, crystallized partially.

The fraction corresponding to the *l*-dihydrochloride in the larger experiment separated very quickly from absolute alcoholic hydrochloric acid on seeding, and was very difficult to filter. After recrystallization from absolute alcohol, to which dry hydrogen chloride was added after cooling, it again separated in very finely divided form, and as the base recovered from the salt showed little tendency to crystallize, further work on this considerable fraction was abandoned.

### O-Ethyl-dihydrocupreicinal

*d*-O-Ethyl-dihydrocupreicinal Hydrochloride.—The reduced solution of 20 g. of ethyl-dihydrocupreicine sulfate<sup>11</sup> was centrifuged from the palladium black, neutralized with sodium hydroxide, and treated with solid sodium chloride until just turbid. The salt slowly crystallized. After several days in the ice-box it was filtered off, washed with 10% salt solution, and recrystallized from water, separating as cream colored prisms and needles. Further recrystallization from absolute alcohol yielded practically white plates containing alcohol of crystallization. The yield was 7.2 g.  $[\alpha]_D^{26}$  of the dried salt was constant at  $+81.1^\circ$  in water,  $c=1.010$ , and the melting point was  $209-210^\circ$  with preliminary softening. The salt is sparingly soluble in water or absolute alcohol at  $0^\circ$ , but dissolves more easily in methyl alcohol. An aqueous solution has a weakly bitter taste and a marked anesthetic action on the tip of the tongue. When treated with sodium bromide it soon deposits the bromide as sheaves and rosetts of minute needles, and yields a nitrate of somewhat similar appearance with sodium nitrate.

*Analyses.* Calc. for  $C_{21}H_{30}O_2N_2.HCl$ : N, 7.40; Cl, 9.36. Found: N, 7.40; Cl, 9.26.

*d*-O Ethyl-dihydrocupreicinal.—An aqueous solution of the salt was made alkaline with sodium carbonate. On letting stand, with occasional rubbing, the base gradually crystallized. When dissolved in alcohol and then well chilled and treated with water until the initial turbidity just redissolved, the base separates on seeding and standing in the ice-box as radiating masses of flat needles. If the recrystallization is attempted at room temperature the crystalline hydrate apparently does not form, and the base comes out oily. When washed with a little chilled 50% alcohol and air dried it comes to equilibrium with 2 molecules of water of crystallization. The hydrate dissolves readily in alcohol or acetone and melts at  $59.5-61.5^\circ$ . When anhydrous the base melts to a semifluid mass at  $56-58^\circ$ , with preliminary sintering and softening, and is completely fluid at  $105-110^\circ$ .  $[\alpha]_D^{24.5}$  is  $+100.2^\circ$  in absolute alcohol;  $c=1.018$ .

*Analyses.* Calc. for  $C_{21}H_{30}O_2N_2.2H_2O$ :  $H_2O$ , 9.53. Found: 9.48. Calc. for  $C_{21}H_{30}O_2N_2$ : C, 73.63; H, 8.84; N, 8.19. Found: C, 73.97; H, 8.66; N, 8.67.

*d*-O-Ethyl-dihydrocupreicinal Dihydrochloride.—This was prepared from the monohydrochloride with alcoholic hydrochloric acid and ether. It forms rosetts of platelets which are extremely soluble in water and rather sparingly so in absolute alcohol at room temperature but easily on heating. It gelatinizes under dry chloroform and dissolves with difficulty. When rapidly heated to  $190^\circ$ , then slowly, it melts with preliminary softening at  $192-194^\circ$  with gas evolution to a yellow liquid.  $[\alpha]_D^{24}$  is  $+149.2^\circ$  in water;  $c=1.045$ .

<sup>11</sup> THIS JOURNAL, 44, 1094 (1922).

*Analyses.* Calc. for  $C_{21}H_{29}O_2N_2 \cdot 2HCl$ : N, 6.75; Cl, 17.08. Found: N, 6.96; Cl, 16.96.

Neither the *l*-base nor any of its salts could be obtained crystalline.

***d*-N-Methyl-O-Ethyl-dihydrocupreicinol.**—*d*-O-Ethyl-dihydrocupreicinol hydrate was treated in dry acetone with an equivalent of methyl iodide. The N-methyl hydriodide which separated as minute rosetts and prismatic needles was converted into the base by addition of sodium carbonate to its aqueous solution. Recrystallized from 50% alcohol, it formed rosetts of long, narrow, glistening platelets which melted slowly at 136.5–137.0° with slight preliminary softening, giving  $[\alpha]_D^{26.5} + 88.2^\circ$  in absolute alcohol,  $c=0.993$ , and greatly resembled the corresponding dihydroquinicinol base in properties and reactions, except for a slightly greater solubility in organic solvents.

*Analyses.* Calc. for  $C_{22}H_{30}O_2N_2$ : C, 74.10; H, 9.05; N, 7.87. Found: C, 74.16; H, 8.93; N, 8.64.

***d*-N,O-Diethyl-dihydrocupreicinol.**—Equimolecular amounts of the base and ethyl iodide were allowed to react in dry acetone, the hydriodide of the diethyl compound separating as sheaves of delicate needles. The base, obtained from the salt as in the preceding case, crystallized on adding a little ether and allowing this to evaporate. It was dissolved in hot 70% alcohol, cooled, and treated with water until just turbid, separating slowly when seeded and aided by the addition of occasional small portions of water as minute, glistening rhombs. The base melts constantly at 110–111° with slight preliminary softening and gives  $[\alpha]_D^{29} + 87.1^\circ$  in absolute alcohol;  $c=0.804$ . In its properties it resembles the methyl homolog, but is even more easily soluble.

*Analyses.* Calc. for  $C_{24}H_{34}O_2N_2$ : C, 74.54; H, 9.25; N, 7.57. Found: C, 74.87; H, 9.46; N, 7.68.

### Summary

Cinchona alkaloids of the cinchonine and quinicine type, reduced with palladium and hydrogen, yield mixtures of stereoisomers of a new type of alkaloids which we have called dihydrochonicinols and dihydroquinicinols. In general the *d*-forms proved easier to isolate. A number of the *d*-bases, one of the *l*-bases, and numerous salts of the *d*- and *l*-forms are described.

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## THE AUTOXIDATION OF ETHYL ETHER

By A. M. CLOVER

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When a glass-stoppered bottle of ordinary ethyl ether is allowed to stand for several months, it is known to acquire oxidizing properties which are usually attributed to hydrogen peroxide or to "ethyl peroxide." When this impure ether is allowed to evaporate in an open vessel, a liquid residue remains which possesses, besides these oxidizing properties, a very pungent odor. The residue completely disappears in time, through evaporation.

Frequent references occur in pharmaceutical literature to explosions<sup>1</sup>

<sup>1</sup> Schär, *Arch. Pharm.*, **225**, 623 (1887). Cleve, *Chem. News*, **63**, 101 (1891); *Pharm. Ztg.*, **34**, 426 (1889). Neander, *Chem. Ztg.*, **26**, 336 (1902).

which have resulted from ether residues. Other impurities including acetic aldehyde and acid are known to be formed in ether on standing and all of these impurities are of importance in connection with the use of ether as a solvent and especially as an anesthetic in medicine. The action of air upon ether appears to be of particular interest because we have here a case of peroxide formation by autoxidation of a very stable substance, whereas from chemical experience we are led to expect such behavior only with unsaturated or highly reducing substances.

Schönbein<sup>2</sup> first noted the formation of an oxidizing substance in ether and this has since been referred to frequently as hydrogen peroxide.<sup>3</sup> Berthelot<sup>4</sup> considered the peroxide of ether to be identical with "ethyl peroxide" which he had obtained by the action of ozone upon ether. Nef<sup>5</sup> assumed that oxidized ether contained diacetyl peroxide.

### The Accumulation of Active Oxygen in Ether

Dunstan and Dymond<sup>6</sup> and also E. v. Neander<sup>7</sup> determined the active oxygen content of certain samples of ether by means of their action upon an acidified solution of potassium iodide. This method has been found to be reliable for quantitative work. A few cubic centimeters of the ether is dissolved in a dilute solution of potassium iodide, acidified with sulfuric acid and the solution is then allowed to stand for 15 minutes. The free iodine is determined with sodium thiosulfate. For very accurate work a control experiment may be used.

Several years ago Mr. R. I. Perkins and the writer first studied the gradual development of ether peroxide<sup>8</sup> by frequently charging cork-stoppered bottles of ether with air. At the end of 5 or 6 weeks the active oxygen content of the solutions reached a maximum which was only about 0.01 *N*. Later, it was discovered that when an ordinary glass-stoppered reagent bottle was partly filled with ether and allowed to stand in a light place there was not only a continuous development of peroxide, but the development took place at a gradually increasing rate.

All ether used in this work was carefully purified by shaking it several times with  $\frac{1}{4}$  volume of water, then allowing it to stand for about a month over 20% sodium hydroxide in amber glass bottles; finally it was distilled. It was desired to remove especially all traces of alcohol

<sup>2</sup> Schönbein, *J. Chem. Soc.*, **4**, 134 (1852); *J. prakt. Chem.*, [1] **52**, 135 (1851).

<sup>3</sup> Buchner, *Chem. Ztg.*, **9**, 691 (1885). Richardson and Fortey, *J. Chem. Soc.*, **69**, 1352 (1896). Kingzett, "Year Book of Pharm." **1876**, p. 554; *Chem. News*, **34**, 135 (1876).

<sup>4</sup> Berthelot, *Compt. rend.*, **108**, 543 (1889); **92**, 895 (1881).

<sup>5</sup> Nef, *Ann.*, **298**, 202 (1897).

<sup>6</sup> Dunstan and Dymond, *J. Chem. Soc.*, **57**, 574 (1890).

<sup>7</sup> Neander, Ref. 1.

<sup>8</sup> This term will be applied to the organic peroxide which, as will be shown, is derived directly by the action of oxygen upon ether.

and aldehyde as these are later formed by decomposition of ether peroxide. The ether was not especially dried. No better method of oxidation could be discovered than the one already described. Glass-stoppered bottles  $\frac{2}{3}$  filled were allowed to stand in a light place without further attention. The reaction is very slow at first and at least 6 weeks is required for the solution to become 0.01 *N* in active oxygen. As the accumulation of peroxide proceeds, the rate of peroxidation increases greatly and during the summer season, providing the heat is not excessive, several per cent. of peroxide is developed at the end of 5 or 6 months. The strength of these solutions is due partly to loss of ether by evaporation.

*Light* has a very important influence upon the peroxidation, but it does not appear to be indispensable. A bottle of purified ether in amber glass was well protected from light and at the end of 6 months no peroxide could be detected. On the other hand, a sample which had not been especially purified, but was free from peroxide, did develop a small amount of the latter under the same conditions. Also, it is a fact that ether sealed in tin cans for use in anesthesia frequently develops peroxide although free from the latter originally. That light is not essential to peroxidation is proved by the following experiment. A glass-stoppered amber bottle was partly filled with ether in which peroxide had been accumulating for some time and the bottle was well protected from light. At the beginning, the solution was 0.125 *N* in active oxygen. At the end of 12 weeks, the ether had evaporated to just about  $\frac{1}{2}$  the original volume but the concentration of peroxide had increased 4-fold to 0.525 *N*. It seems that light is much more important in starting the peroxidation than it is at a later stage, and it has been found that bottles of ether which had started to oxidize during the winter season of short daylight progressed much more slowly than those started in the summer season.

*Direct sunlight* was found to have a favorable influence upon the accumulation of peroxide up to a certain point, and with further exposure there was a decrease. It will be shown later that ether peroxide is broken down by light and it is probably because of the pronounced decomposition by direct sunlight that it was found impossible to obtain solutions of any considerable strength in this way.

**Catalytic Action of Acetaldehyde.**—An explanation was desired of the progressive increase in the rate of peroxidation and attention was directed to the influence of decomposition products of the peroxide. It was discovered that with samples of ether which had reached a fairly rapid rate of peroxidation, the latter came to a standstill if a portion of the ether were volatilized, and the conclusion was drawn that the influence was due to a volatile product. Experiments showed that carbon dioxide, carbon monoxide, ethylene and alcohol were without effect. Acetaldehyde, which is known to be one of the products of spontaneous decomposition,



was also tried. When this substance was added to pure ether, one part in 1000, the amount of peroxide found at the end of 2 months was about twice that which had developed in the pure ether. When 0.5% of aldehyde was added the effect was decidedly greater, and it appears from the experiments performed that such an amount would be necessary to explain the rapid accumulation of peroxide in ether after long standing.

**Development of Hydrogen Peroxide.**—Inasmuch as the peroxide contained in ether has been so frequently referred to as hydrogen peroxide, it is of first importance to determine whether the latter substance is a primary product of oxidation, as has been frequently assumed, or whether it is the result of a secondary reaction. It is also important to determine to what extent hydrogen peroxide is present along with ether peroxide and to be able to separate the two.

**The Chromic Acid Test.**—This method of detecting traces of hydrogen peroxide in ether is capable of great delicacy if care be taken to use only a limited amount of sulfuric acid. Hydrogen peroxide to the extent of 0.001% may be detected. Ether peroxide does not respond to this test.

A great many samples of ether have been tested from time to time during the course of oxidation and in no case has it been possible to obtain a positive test for hydrogen peroxide before the end of 3 or 4 months. Usually, at this time there has accumulated in the solution from 0.25 to 0.5% of ether peroxide. The amount of hydrogen peroxide increases slowly with time, but it has never been found to be more than a few per cent. of the amount of ether peroxide. Later it will be shown that ether peroxide reacts slowly with water to form hydrogen peroxide and this reaction, which may be assumed to take place to a very limited extent in ether solution, will account for the hydrogen peroxide. It appears certain that *hydrogen peroxide is not a primary product of oxidation*.

A confirmation of the conclusion drawn from the chromic acid test may be obtained by shaking out oxidized ether with water. Hydrogen peroxide may be completely removed in this way because it is a great deal more soluble in water than it is in ether. The ether peroxide, on the other hand, is more soluble in ether than in water and by repeated extractions an approximate separation of the two may be effected.

### Ether Peroxide

Along with hydrogen peroxide, there is developed in the oxidized ether a relatively small amount of acetic acid.<sup>9</sup> Alcohol in considerable quantity and also aldehyde are formed as secondary products, as will be shown later. Also, it is likely that derivatives of the above substances are present. These secondary or decomposition products of ether peroxide may be easily removed and the primary product of peroxidation may be obtained in a practically pure state as follows.

<sup>9</sup> Richardson and Fortey, Ref. 3.

A sample of oxidized ether which had stood about 6 months was about 0.35 *N* in active oxygen. It was shaken out twice with  $\frac{1}{4}$  volume of water and then gave no test for hydrogen peroxide with chromic acid. The ether was dried by means of anhydrous sodium sulfate. Portions of a few cubic centimeters each of the solution were removed to small weighed flasks and the weights of residues obtained after they had been allowed to remain in a continuous vacuum for different periods of time. In each case a determination of the active oxygen content of the residue was made in the usual manner using a solution of potassium iodide acidified with sulfuric acid. The ether solution was about 0.3 *N* in active oxygen and approximately 4 cc. was removed for each experiment.

Expt.	In vacuum Min.	Wt. of residue G.	0.1 <i>N</i> Thio- sulfate Cc.	Active oxygen %
I .	15	0.0638	10.6	13.29
II	25	0.0526	9.65	14.67
III	55	0.0456	8.45	14.82
IV	100	0.0336	6.25	14.88
V	300	0.0003	.00	..

Calculated active O for  $C_4H_{10}O_2 = 15.09$

In Expt. V the vacuum was maintained for half a day until all odor was gone. No more peroxide was found to be present although apparently a trace of non-volatile matter remained.

The above experiments were carried out in the summer of 1920. A year later an attempt was made to duplicate them with a sample of ether which had stood for 4 or 5 months. During the later 2 months the temperature was unusually high and peroxide had not accumulated as rapidly as had been expected; also it was found to be contaminated with a few per cent. of non-volatile matter. In one sample the active oxygen was found to be 13.75%. After correcting for non-volatile matter it was 14.3%.

Recently, the oxidation of a sample of pure ether has been hastened by the addition of about 0.5% of aldehyde. At the end of 6 weeks, the solution was 0.15 *N* in active oxygen. Acetic acid was present to the extent of about 0.1%. There was no evidence of the presence of peracid. The ether solution was shaken well with  $\frac{1}{3}$  of its volume of dil. sodium hydrogen carbonate solution and was then allowed to evaporate to about  $\frac{1}{3}$  volume. After the solution had been thoroughly dried over sodium sulfate the residue was analyzed as usual. A residue of 0.0422 g. obtained after the sample had remained in a vacuum for 1 hour required 7.3 cc. of 0.1 *N* thiosulfate solution. The non-volatile residue obtained from an equal amount of the ether solution was 0.0028 g. After correcting for the residue the active oxygen was found to be 14.82%.

Ether peroxide is miscible with water, alcohol, ether and acetone and

has a limited solubility in benzol, chloroform and petroleum ether. The boiling point is unknown, as no attempt was made to distil it on account of the great danger involved. It is somewhat volatile. When the solvent is mostly removed from a solution in ether nearly 10% of the peroxide also passes off. This decided volatility shows that it has the simple formula, only 1 molecule of ether or 2 ethyl groups being involved. It has a very irritating taste and odor and is also very irritating to the skin. It yields iodoform with alkali and potassium iodide. When the peroxide is dissolved in an excess of sodium hydroxide the active oxygen gradually disappears from the solution and, at the end of an hour, it has become dark yellow in color. On heating this solution and then acidifying it, a resinous substance is precipitated. When the acidified product is subjected to distillation, the presence of alcohol is shown by the iodoform test.

The following tests were made with a 6% water solution of the peroxide which was free from hydrogen peroxide and ether. The action on platinum black is very feeble when compared to that of hydrogen peroxide. Neither ferric chloride nor manganous chloride shows any catalytic effect upon the active oxygen, but with manganese dioxide and silver oxide oxygen is freely evolved. There appears to be no effect produced by either mercury or finely divided silver. Unlike hydrogen peroxide, it colors both guaiacum and benzidine directly. No precipitate is produced by barium hydroxide and as has already been pointed out, it gives no coloration with chromic acid. In the latter case, care must be used in restricting the amount of sulfuric acid or sufficient hydrogen peroxide will be formed by hydrolysis to respond to the test.

The *ratio of distribution* of ether peroxide between water and ether has already been stated to be very different from that of hydrogen peroxide. Walton and Lewis<sup>10</sup> determined this ratio for hydrogen peroxide at 25° and found the coefficient to be 9.11 when the water contained about 5% peroxide and 8.25 with a solution which was nearly 10% peroxide. The writer has tried more dilute solutions at about the same temperature. With aqueous solutions of 1% and 2.8% of hydrogen peroxide, a coefficient of approximately 16 was obtained in each case. The peroxide was determined through its action on potassium iodide in acid solution. Equal volumes of the two solvents were used. The coefficient for ether peroxide has been found to vary between 1.70 and 2.0 in different experiments, the peroxide being more soluble in ether than in water. Ether solutions of peroxide varying in strength from 0.05% to 0.5% were used.

The *acidic nature* of ether peroxide is worthy of note. This is shown by the fact that the ratio of distribution between ether and water is greatly changed by the presence of alkali, much more of the peroxide being present in the alkaline solution.

<sup>10</sup> Walton and Lewis, *THIS JOURNAL*, 38, 633 (1916).

### Spontaneous Decomposition of Ether Peroxide

Attention has already been directed to the formation of a small amount of hydrogen peroxide which is probably the result of a hydrolytic reaction. Ether peroxide, like other organic peroxides, might be expected to be unstable and especially in solution and under the influence of light to break down into simpler substances. This is found to be a fact. The percentage decomposition of a dilute solution is much greater than that of a strong solution. When protected from light the peroxide also decomposes but more slowly than upon exposure.

A solution (about 0.3 *N*) was exposed to the action of diffused light in a flint-glass bottle with a cork stopper inserted as tightly as possible. After standing for 2 weeks during the month of December, the stopper was removed and there was a continuous evolution of gas lasting several minutes. The solution had lost  $\frac{1}{2}$  of its strength. A fresh stopper was inserted and the decomposition allowed to continue for 4 weeks longer when the strength was found to be less than  $\frac{1}{2}$  of the original. Six weeks later, all but 10% of the original peroxide had disappeared and gaseous products continued to be formed.

Another experiment of a similar kind was carried out. Before the removal of the stopper the bottle was cooled in ice water and a stopper containing a capillary tube was inserted so that the gas which escaped as the bottle again came to room temperature could be collected. The presence of a determinable quantity of carbon dioxide was shown by passing the gas through baryta water. By means of water the gas was washed practically free from ether. There was no further decrease in volume on standing over bromine water or a solution of cuprous chloride. The residual gas after removal of carbon dioxide and ether burned with a blue flame and was undoubtedly methane.

The ether solution in which less than 10% of the original peroxide now remained was subjected to a slow distillation from a flask which was immersed in a vessel of warm water. The distillate was redistilled to remove all peroxide as the latter is somewhat volatile. The product now gave a heavy iodoform test and also responded readily to the test for aldehyde with ammoniacal silver nitrate. When shaken with a 10% solution of potassium hydroxide a yellow color appeared in a few minutes.

The experiment was repeated with a solution 0.45 *N* in active oxygen. The bottle stood from February 11 to April 19 and the stopper was removed several times to relieve the pressure. The gas was tested with the same results as before. On April 19 the amount of peroxide was only 3% of the original. About 100 cc. of the ether was slowly distilled as before. The first portion of the distillate was tested for aldehyde with the same result as before. The second portion, which was about  $\frac{1}{2}$  of the total, was dried over potassium carbonate, then treated with 1.5 g. of *p*-nitrobenzoyl chloride. After 2 days the ether was evaporated. From the residue, after treatment with sodium carbonate solution, there was obtained more than 0.5 g. of the ethyl ester of the above acid; m. p. 56° (crystallized from petroleum ether).

Berthelot<sup>11</sup> demonstrated the formation of *methane* by the action of air upon ether which had been exposed to direct sunlight for several weeks. Berthelot first calls attention to the fact that alcohol is also one of the products formed. The methane was obtained mixed with the residual nitrogen of the air and as the author does not state the experimental

<sup>11</sup> Berthelot, *Compt. rend.*, 129, 627 (1899).

basis for his conclusion that methane is formed, it must be assumed that an analysis of the gas was made. No carbon dioxide was found.

The *development of acetic acid* in ether has been found to be very much slower than that of peroxide. Even after several months' oxidation the amount of acid, as determined by titration, is not over a few per cent. of the amount of peroxide in the solution. After long standing of an ether bottle during which time a large part of the ether had evaporated, the acid content has been found to be as high as 1%. It does not seem likely that the acid is a direct product of decomposition of the peroxide, and its presence may be accounted for by autoxidation of aldehyde. Experiment has shown that during the decomposition of peroxide in tightly stoppered bottles the increase in acidity was relatively very small in proportion to the amount of peroxide decomposed, and this change likewise could be accounted for by autoxidation of aldehyde.

### Action of Dilute Acid on Ether Peroxide

When the peroxide is dissolved in water and the solution allowed to stand, hydrogen peroxide is slowly formed, as shown by the chromic acid test. After several weeks the greater part of the active oxygen is present as hydrogen peroxide, this fact being shown by the ratio of distribution of the active oxygen when the water solution is shaken with pure ether. The formation of hydrogen peroxide is greatly facilitated by the presence of mineral acid and, in fact, the complete conversion of the active oxygen may be brought about by this means in a short time.

Four hundred and fifty cc. of oxidized ether, which was about normal in active oxygen and, accordingly, a little more than 5% in ether peroxide, was shaken out with 50 cc. water and the water extract preserved. The ether was distilled in a vacuum nearly to completion. One hundred cc. of water was then added and this solution was freed from ether *in vacuo*. The distillation in a vacuum was continued by immersing the distilling flask in a vessel of water at 50°. About 15 cc. was distilled, which presumably contained most of the remaining alcohol. The solution in the flask now contained about 90% of the active oxygen present at the beginning, or about 22.5 g. of ether peroxide. A few drops of dil. sulfuric acid were added and the solution was allowed to stand at 60° for 2 or 3 hours after which it was subjected to distillation at ordinary pressure. A strong odor of acetaldehyde was noted. About  $\frac{1}{3}$  of the liquid was distilled and the distillate was treated with potassium carbonate, whereupon about 15 cc. separated to the top. The liquid was dried further with fresh anhydrous potassium carbonate and became colored on standing. On distillation it did not show a constant boiling point although most of it passed over below 80°. The product is mostly alcohol contaminated with derivatives of acetaldehyde. Probably paraldehyde and the mono-acetal,  $\text{CH}_3\text{CH}(\text{OH})(\text{OC}_2\text{H}_5)$ , are present.

After distilling the product of hydrolysis of the peroxide, there remained a solution of hydrogen peroxide which was found to be of nearly 12% strength. A portion of it was converted directly into succinic acid peroxide as follows. Ten cc. of the solution was diluted with 5 cc. of water and 5 g. of small crystals of succinic anhydride added. The mixture was shaken frequently during the course of 45 minutes. After filtering, washing and drying, about 1.5 g. of pure succinic acid peroxide was obtained.

**Analysis.** Calc. for  $C_2H_5O_8$ : O (active), 6.84. Found: 6.76.

The water extract of the original peroxide solution was then diluted with an equal volume of water and this subjected to distillation at reduced pressure, the temperature of the heating bath being about  $60^\circ$  to  $65^\circ$ . Approximately  $\frac{1}{4}$  of the total was distilled. This distillate was found to contain only a negligible amount of peroxide and was partly redistilled. This last distillate gave a decided iodoform reaction, but no tests for aldehyde. When it was treated with solid potassium carbonate, about 1 cc. of alcohol separated. The latter was dissolved in 15 cc. of alcohol-free ether which had been dried over anhydrous potassium carbonate. About 3 g. of *p*-nitrobenzoyl chloride was added and, after standing several days, nearly 3 g. of the ethyl ester was obtained; m. p. after recrystallization from alcohol,  $55-56^\circ$ .

In another experiment the hydrolysis of the peroxide was allowed to proceed in acid solution at  $45^\circ$  and no change was noted in the general result. In this case it was ascertained that during the hydrolysis there was little, if any, loss in active oxygen. A small volume of the solution at the beginning and at the end of the experiment gave practically the same values. The formation of a considerable amount of aldehyde or its derivatives was shown by the formation of resinous matter on treating the distillates with caustic alkali.

**Acetic Peroxide and the Theory of Nef.**—If acetic peroxide were present in oxidized ether its identification would be relatively simple as it soon changes to acetic peracid when dissolved in water, and the latter substance is characterized by the rapidity of its action upon potassium iodide. Iodine is precipitated at once from a very dilute solution of the former.<sup>12</sup> At no time has it been possible to detect this substance. Again, the theory of Nef assumes that hydrogen peroxide is formed as a direct product of oxidation and there is no experimental evidence for such an assumption.

**"Ethyl Peroxide."**—Without doubt the idea of Berthelot concerning the structure of this substance was that 2 molecules of ether take on an extra atom of oxygen just as barium oxide does at a high temperature, and that in the formation of "ethyl peroxide,"  $(C_2H_5)_4O_3$ , no change takes place in the ethyl groups. Since the time of Berthelot's publication Baeyer and Villiger<sup>13</sup> have synthesized diethyl peroxide,  $(C_2H_5)_2O_2$ , an ether-like body which, unlike Berthelot's product, is very difficult to reduce and does not react with water to form hydrogen peroxide. Harries<sup>14</sup> also studied the action of ozone on dry ether at low temperature and subjected the product to distillation in a vacuum. A peroxide-containing distillate was obtained, but the results of elementary analyses were not concordant nor were they close to those required for Berthelot's formula. We may conclude from the literature that "ethyl peroxide" possibly consists, at least partly, of ether peroxide, but this is not strictly proved. There does not appear to be much of an experimental basis for the formula of Berthelot.

<sup>12</sup> Baeyer and Villiger, *Ber.*, 33, 1575 (1900).

<sup>13</sup> Baeyer and Villiger, *ibid.*, 33, 3387 (1900).

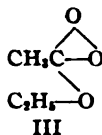
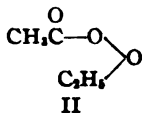
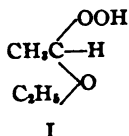
<sup>14</sup> Harries, *Ann.*, 343, 375 (1905).

### The Structure of Ether Peroxide

The following facts are to be considered. (A) The active oxygen content of the pure peroxide is approximately that required for a substance formed by the addition of one molecule of oxygen to one molecule of ether,  $\frac{1}{2}$  of the added oxygen being active. (B) The peroxide is formed directly by the action of oxygen upon ether. (C) It is volatile. (D) It decomposes, especially under the influence of light, with the formation of carbon dioxide, methane, aldehyde and alcohol. (E) It reacts with acidified water to yield hydrogen peroxide quantitatively. Alcohol and aldehyde are also formed in considerable quantity. (F) Ether peroxide is acidic.

That the ethyl group is directly attacked in the peroxidation is proved by (E), since aldehyde could not be formed here as the result of a secondary oxidation, except at the expense of active oxygen. That only one ethyl group enters into reaction with oxygen is shown by both (D) and (E) because in both cases considerable quantities of alcohol are formed. That the hydrogen of only one carbon atom has been affected is shown by the formation of methane (D). The acidic nature of the peroxide indicates the presence of an OOH group, for both the mono-alkyl and mono-acyl derivatives of hydrogen peroxide are known to form salts.

If hydrogen is *not removed*, but merely displaced, we have the following structure (I) which is  $\alpha$ -ethoxyethyl hydrogen peroxide.



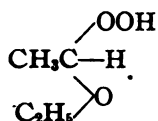
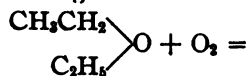
If hydrogen is *removed*, ethyl peracetate (II) might be formed which differs from (I) by having 2 atoms less of hydrogen.

Baeyer and Villiger<sup>15</sup> state that the odor of the latter substance is similar to chloride of lime. This cannot be said of ether peroxide. Also according to Baeyer and Villiger, ethyl peracetate yields ethyl hydrogen peroxide upon treatment with alkali, and the latter has been shown by the same authors to be stable in alkaline solution. Ether peroxide, on the other hand, when treated with alkali soon loses its active oxygen and is converted into a resinous product. Such a very improbable structure as (III) which would be isomeric with ethyl peracetate could not yield aldehyde on hydrolysis except by loss of active oxygen. Also, it would be difficult to explain the formation of methane and alcohol by the decomposing action of light.

Formula I is in agreement with all the experimental facts and therefore represents the true structure of ether peroxide. Accordingly the latter is formed simply by the displacement of one hydrogen atom of a methylene

<sup>15</sup> Baeyer and Villiger, *Ber.*, 34, 746 (1901).

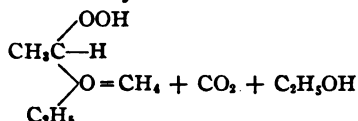
group by one molecule of oxygen, the net result being the addition of a molecule of oxygen to a molecule of ether.



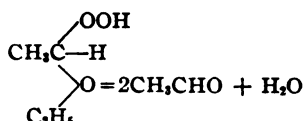
This conclusion is strengthened by the highly probable theory of Baeyer and Villiger<sup>16</sup> concerning the autoxidation of benzal-

hyde which takes place as follows:  $\begin{array}{c} \text{H} \\ \diagup \\ \text{C}_6\text{H}_5\text{C}=\text{O} \end{array} + \text{O}_2 = \begin{array}{c} \text{OOH} \\ \diagup \\ \text{C}_6\text{H}_5\text{C}=\text{O} \end{array}$ .

Under the influence of light the decomposition of ether peroxide takes place in two ways.

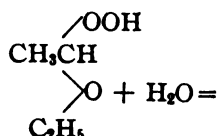


(1)

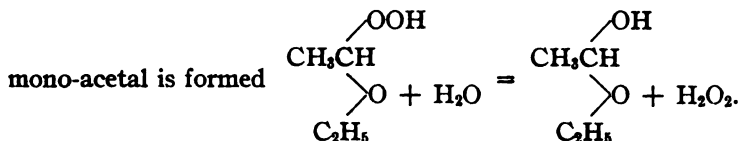


(2)

The action of acidulated water is as follows:



$\text{CH}_3\text{CHO} + \text{C}_2\text{H}_5\text{OH} + \text{H}_2\text{O}_2$ . It is possible that to some extent the



The results obtained with ethyl ether have naturally suggested a study of other ethers and a number of these have been tried in a preliminary way. All have been found to undergo peroxidation. The rapidity of peroxide formation appears to increase with increasing size of the molecule although a pronounced progressive increase in the rate like that with ethyl ether has not been observed with butyl or amyl ethers. Ethers containing a benzyl group oxidize more rapidly than those of the aliphatic group and in the case of benzyl methyl ether, peroxidation takes place to the extent of 20-25% in the course of a month. A study of the peroxidation of ethers is being continued.

### Summary

Ether absorbs oxygen from the air, very slowly at first with the formation of a peroxide by direct addition. The rate of peroxidation becomes

<sup>16</sup> Ref. 12, p. 1569.



much greater in time due to the catalytic influence of acetic aldehyde, the latter being formed by spontaneous decomposition of the peroxide.

Ether peroxide has been prepared in sufficient quantity to permit a study of its properties and decomposition products, and a structural formula has been assigned to it.

DETROIT, MICHIGAN

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[CONTRIBUTION FROM THE RESEARCH DEPARTMENT OF THE BARRETT COMPANY]

## PRELIMINARY STUDY ON THE FORMATION OF MALIC ACID

By JOHN MORRIS WEISS AND CHARLES R. DOWNS

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Until comparatively recently very little maleic, fumaric and malic acids have been available to the chemist for investigation. The difficulty of obtaining even moderate quantities from natural sources discouraged work along these lines and a considerable portion of the data in the literature is inaccurate and misleading owing to the meagre quantities with which chemists had to deal. The authors<sup>1,2</sup> described a method for the synthesis of maleic acid by the partial oxidation of benzene in the presence of a catalyst which has resulted in ample supplies of material becoming available. We desire here to present some results on the reactions of maleic, fumaric and malic acids in respect to the transformation of maleic acid to fumaric acid and malic acid and of fumaric acid to malic acid.

The earliest work on the transformation of fumaric acid to malic acid was carried on by F. Loydl<sup>3</sup> who heated fumaric acid with dil. caustic soda solution at about 100° for 100 hours and in this way converted about 52% of the fumaric acid into malic acid. He states that the malic acid is deliquescent in a moist atmosphere, optically inactive and decomposes at 200° into water and fumaric acid without giving a trace of maleic acid.

E. Yungfleisch<sup>4</sup> claims that malic acid with a small amount of water is converted almost completely to fumaric acid when heated in a sealed tube at 180°. As the proportion of water is not stated, the results are of questionable value. He further states that at 150° in the presence of a large excess of water fumaric acid is converted in part to malic acid which latter is identical with inactive malic acid.

A. Pictet<sup>5</sup> repeated the latter part of Yungfleisch's work on the preparation of malic acid. He gives no experimental details of the reaction but describes the product as non-deliquescent and decomposing at 135°, giving maleic anhydride and water in the distillate and fumaric acid in the residue. He decided that he obtained a different product from that of Loydl,<sup>3</sup> not realizing that the latter probably obtained an impure product by the method he employed, and concluded that there were probably two varieties of inactive malic acid corresponding to racemic and meso-tartaric acids.

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<sup>1</sup> Weiss and Downs, *J. Ind. Eng. Chem.*, **12**, 228 (1920).

<sup>2</sup> U. S. pats. 1,318,631; 1,318,632; 1,318,633; 1,377,534.

<sup>3</sup> Loydl, *Ann.*, **192**, 80 (1878).

<sup>4</sup> Yungfleisch, *Bull. soc. chim.*, **30**, 147 (1878).

<sup>5</sup> Pictet, *Ber.*, **14**, 2648 (1881).

H. J. Van't Hoff, Jr.<sup>6</sup> followed the Loydl procedure using maleic acid but gives no details. He concludes that the malic acid obtained is the same as that he had previously obtained<sup>7</sup> from monobromosuccinic acid.

Tanatar<sup>8</sup> made the statement that maleic acid could be completely converted into fumaric acid by heating with water.

This statement was denied by Skraup<sup>9</sup> who published a rather extended account of experimental work in this connection. He brought out the following facts. All acids to a greater or lesser degree aid the reaction of the change of maleic acid to fumaric acid. Maleic acid heated under pressure with water gives fumaric acid under conditions where malic acid is not converted into fumaric acid, thus allowing the conclusion that malic acid is not an intermediate product in the transition from maleic to fumaric acid. He shows that at the lower temperatures, starting with maleic acid, an equilibrium exists among all three acids, while at the higher temperatures only between malic and fumaric acids. He also repeated Loydl's experiments<sup>8</sup> using both maleic and fumaric acids as raw materials, but slightly changed the procedure so as to insure a purer product. He obtained an inactive malic acid from each and showed that the behavior on heating both these acids as well as active malic acids was identical and different from that stated by Loydl. Heated rapidly to 200° the dry acids gave maleic and fumaric acids in about equal amounts, but heated slowly they formed fumaric acid to the extent of about nine times the quantity of maleic acid. Maleic acid heated alone at 130° gave fumaric acid and malic acid.

Tanatar<sup>10</sup> replies to Skraup and states that a 10-30% aqueous solution of maleic acid heated in a sealed tube for 2 hours at 200-220° is practically entirely converted into fumaric acid, and under like conditions malic acid is left unchanged. Tanatar admits, however, that his experiments were only qualitative and that small quantities only were used, so that we can fairly conclude that his results are unreliable. The article is long and for the most part polemical.

A reply was made by Skraup<sup>11</sup> which is largely polemical in nature but gives the results of a few more experiments on heating maleic acid alone and in the presence of benzol. In the former case, all three acids were found in the reaction product and in the latter the same general results were obtained except that the greater portion of the unchanged maleic acid was isolated from the benzol solution as the anhydride.

Later Tanatar<sup>12</sup> replied again but the article is entirely polemical in nature.

In general, with regard to the literature we may say that in most cases the amounts of materials used were too small for accurate results and there is considerable doubt as to the purity of the substances employed. Therefore, our real knowledge of these reactions up to the present has been in many ways inaccurate and certainly incomplete.

**Analytical Methods.**—Since the determination of the equilibria of these three acids in water solution was dependent upon a knowledge of the composition of the water solutions, methods of analysis had to be developed.

It was early found that fumaric acid could easily be determined within

<sup>6</sup> Van't Hoff, Jr., *Ber.*, **18**, 2713 (1885).

<sup>7</sup> Ref. 6, p. 2170.

<sup>8</sup> Tanatar, *J. Russ. Phys. Chem. Soc.*, **22**, 1, 310-312 (1890).

<sup>9</sup> Skraup, *Monatsh.*, **12**, 107 (1891).

<sup>10</sup> Tanatar, *Ann.*, **273**, 31-55 (1893).

<sup>11</sup> Skraup, *Monatsh.*, **14**, 501 (1893).

<sup>12</sup> Tanatar, *Ber.*, **27**, 1365 (1894).

a reasonable degree of accuracy when the temperature of the water solutions of malic acid was known, due to its slight solubility. The solubility of fumaric acid was determined to be 0.7 g. per 100 g. of water at 25°. All determinations of fumaric acid were therefore made at 25° and provided sufficient agitation and time to assure solution equilibrium.

Although considerable work has been done on the salts of malic and maleic acids, no satisfactory method of analysis has been developed to determine quantitatively these acids mixed in water solution.

It was, however, found that when the amount of maleic acid in solution was very small the bromine method, described below, was quite accurate.

Wislicenus<sup>13</sup> reported that maleic acid in water solution is transformed into fumaric acid by the use of bromine and iodine but not by chlorine in the presence of light. In no case did the halogens attack the double bond. Since little information was available concerning the quantitative relations of this reaction, a study was undertaken to determine whether it was capable of development into a method for the quantitative estimation of maleic acid in the presence of malic acid.

During our investigation, different sources of light, that is, sunlight, an incandescent bulb and a Hanovia mercury vapor quartz light, were tried for this purpose. The speed of reaction under the effect of the last was by far the greatest and since it appeared that a long time of contact of the bromine and the acid resulted in the formation of by-products a quick acting test was desirable.

The method of procedure finally adopted was as follows.

The water solution of about 40% malic acid containing small amounts of maleic acid was saturated with fumaric acid by agitating at 25° in a thermostat. When this solution contained only malic and maleic acids, an excess of solid fumaric acid was added thereto. In the solutions taken from the bombs during the equilibrium experiments, there was always an excess of solid fumaric acid.

After saturation of the solution with fumaric acid had become complete, the undissolved fumaric acid was filtered off, care being taken to maintain the temperature of the solution at 25° by immersing the filtering apparatus in the thermostat.

The clear filtrate was placed in transparent fused quartz test-tubes of about 12 mm. in diameter and 15 cm. long. A very small amount of liquid bromine, that is, about 0.005 cc., was run in from a capillary tube and the quartz tube was placed under a Hanovia ultra-violet mercury vapor lamp at a distance therefrom of about 11 cm. The time of exposure was about 10 minutes, after which the liquid was decanted as completely as possible from the remaining liquid bromine at the bottom of the tube. The solution was placed in a dry bottle, iced externally until

<sup>13</sup> Wislicenus, *Ber.*, 29, 1080 (1896).

seed crystals of fumaric acid separated and then the bottle was placed in the thermostat as before at 25°. It was found and checked by a number of observers that if the crystals of fumaric acid did not dissolve there was at least one part of maleic acid per thousand parts of malic acid in the original solution.

Since the object of this investigation was the study of the equilibrium at the higher temperatures, the conditions were such that there were only very small amounts of maleic acid in the resultant products. The test as described above is not quantitatively accurate for the estimation of all percentages of maleic acid, but was satisfactory for the purposes of the experiments described in the present paper.

Should the equilibria at lower temperatures be investigated, an accurate method for the analysis of malic-maleic acid mixtures in water solution would have to be developed.

### Apparatus and Procedure for the Conversion Experiments

A water solution of the acid was placed in a thin-walled Pyrex glass tube having a length of 18–19 cm. and an external diameter of 3 cm. The glass tube was then inserted into a stout steel bomb which was about 30 cm. long and 5 cm. in diameter (external dimensions). The bore of the steel tube was just large enough so that the glass tube rested easily therein. A little water was placed between the glass tube and the steel bomb wall to insure good heat transference. A glass cap rested upon the open end of the glass tube to prevent the acid solution from becoming contaminated with iron rust. The bomb was closed by screwing a steel plug into the open end, an aluminum gasket being used to make a tight joint.

The steel bomb with its contents was then suspended in an upright position in an agitated oil-bath which had previously been heated to the desired temperature. After the bomb had been heated for the desired length of time, it was lifted from the oil-bath and, after the excess oil was removed from it, immersed in a vessel of cold water. When thoroughly cooled the bomb was opened and the glass tube removed.

The contents of the glass tube were then cooled to 25°, filtered with suction and the fumaric acid washed quickly with a small amount of cold water. It was found that when this washing was done sufficiently rapidly the amount of fumaric acid dissolved in the wash water was negligible. The washings and original filtrate were combined and titrated with standard caustic alkali solution. The fumaric acid which was filtered off was dried at 110° and weighed. Correction was finally made for the amount of fumaric acid dissolved in the malic acid solution by applying the solubility of fumaric acid (0.7 g. of acid in 100 g. of water at 25°) to the original amount of water taken.

The filtrate containing the malic acid, small amounts of fumaric acid and maleic acid, if any, was evaporated at a low temperature under a vacuum to 20 cc. volume and cooled to 25° to precipitate fumaric acid. Low temperature evaporation was used to prevent any further reverse conversion of malic acid to fumaric acid, as it had been shown that even heating a solution of malic acid below 100° gave no fumaric acid. The solution was then placed in a thermostat as directed under the test for maleic acid given above. Although this test is not quantitative for various amounts of maleic acid, it is evident that only very small errors could have arisen in this work as the amount of maleic acid was always below 0.5% of the total acids present.

A great many experiments have been made using various sizes of autoclaves, but since the results in general check those obtained in these small bombs, no description of them is considered of interest here. The only factor of importance in treating large volumes of solution which differed from the results given in this paper is that of the time of heating. Agitation of large volumes, particularly where solid fumaric acid is present, is needed to hasten the final equilibrium.

**Preparation of Materials.**—The maleic acid was prepared by dissolving in distilled water maleic anhydride which was made from high purity maleic acid by several redistillations under high vacuum. It was preserved ready for use in a stoppered bottle in a desiccator. It gave a solidifying point of 52.6°, and titrated as 99.1% pure maleic anhydride.

The inactive malic acid was carefully prepared by autoclaving maleic acid, followed by careful purification to remove fumaric acid. It contained no fumaric acid and no maleic acid as shown by the bromine test. It titrated 99.6% pure.

The fumaric acid was made by recrystallizing high purity fumaric acid several times from water and titrated 99.8% pure.

The *levo*-malic acid was a commercial<sup>14</sup> product supposedly made from maple "sugar sand." It titrated 95.15% pure malic acid.

### Experimental Results<sup>15</sup>

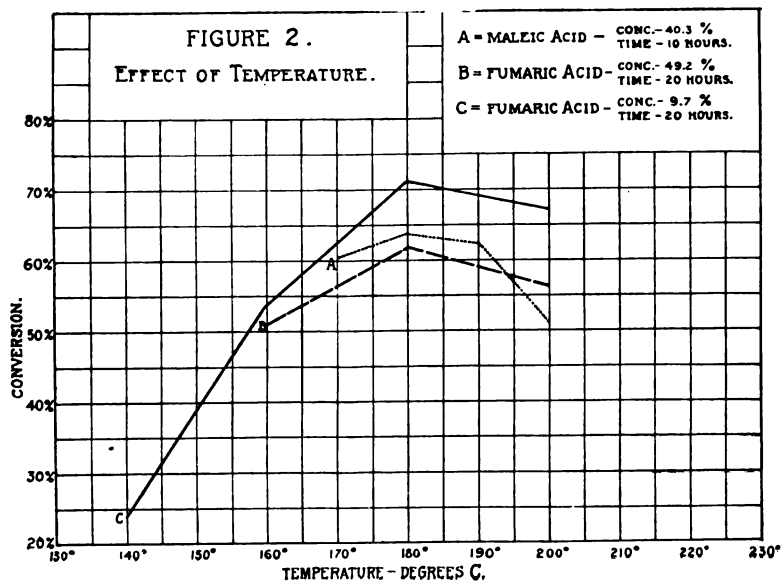
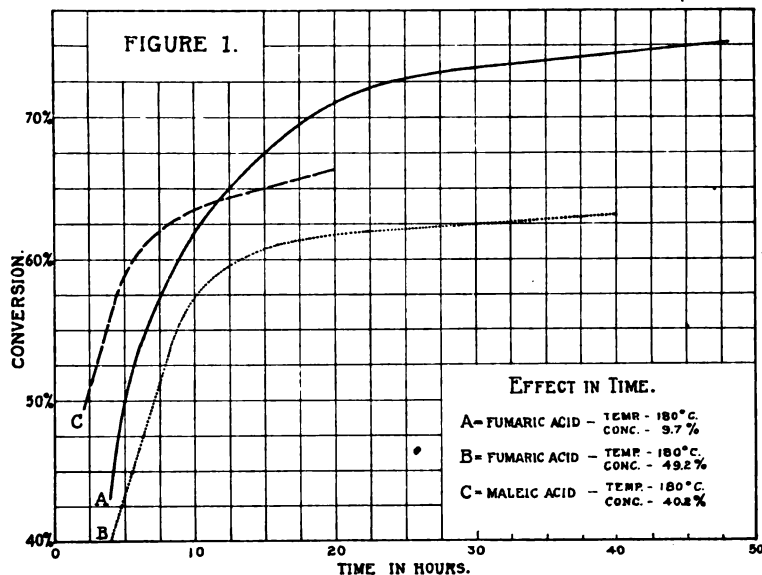
The main results are shown graphically in Figs. 1, 2 and 3 covering the effect of time, temperature and concentration on the equilibrium. The conversion is expressed as the percentage of either maleic or fumaric acid converted to malic acid. The results used in the curves are the average of two check determinations. When fumaric was used in the experiments, we were never able to detect maleic acid in the products. In the maleic series at the lower temperatures and times, maleic acid was

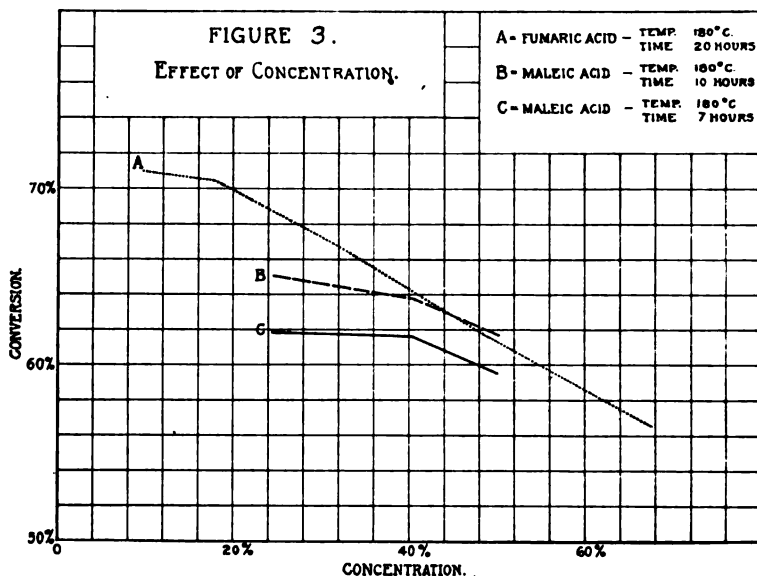
<sup>14</sup> Eastman Kodak Company.

<sup>15</sup> Much of the work on this problem was carried out by Messrs. F. Boettner, H. P. Corson and E. Wolesensky of The Barrett Company Research Laboratory staff,

found in the product but the amount never exceeded 0.5% of the acid used initially.

When maleic acid is used, we have a homogeneous system throughout but with fumaric acid without agitation the insolubility probably retards the reaction speed to a certain extent. However, it was proved that at





least at the conclusion of the heating period in our experiments we had a homogeneous system, that is, all products were in solution.

Some further tests were made heating inactive malic acid with water to see if approximately the same end-point were reached. At a concentration of 40% and a temperature of 180° after 7 hours 25.1% of malic acid had changed to fumaric; after 10 hours, 29.1% had changed. The reaction appears to approach the same end-point as when converting fumaric acid to malic acid.

A like test was carried out on the *levo*-malic acid obtained from maple sugar sand. Two runs were made at 180° for 10 hours at a 40% concentration and gave results of 26.4 and 27.2% conversion to fumaric acid. The residual malic acid was compared with the original by polariscope methods.

300 mm. tube, 25°, 10% solutions		$[\alpha]_D^{25}$
Original malic.....	0.53°	1.8°
After pressure treatment.....	0.07°	0.24°
Ordinary inactive malic.....	0.02°	0.07°

It may be seen that here also we are approaching the same end-product.

There were also a few experiments in which maleic acid was heated alone, without the presence of a solvent. Four flasks containing maleic acid were heated in a glycerine-bath at 140°. In 5 minutes all the maleic acid was melted. Shortly afterward, fumaric acid crystals began to form in the molten mass and fall to the bottom.

Flask	Time Min.	Fumaric acid formed %	Malic acid formed %
1	5	10	1
2	15	17	3.3
3	45	26	4.0
4	95	41	6.0

This seems to show that malic acid is not an intermediate product, for otherwise there would be a period where malic acid predominated in amount over the fumaric acid.

On the basis of the results obtained we at first attempted to calculate the physical-chemical equilibrium constants but soon found that the methods of manipulation and our lack of certain essential facts made it impossible to make such calculations with even an approximate degree of accuracy. We need only call attention to the fact that we did not have knowledge of the density of the final product at the temperatures and pressures used, and that due to the empty space in the bomb above the charge there was a certain amount of water volatilized from the solution during the operation, and as this was an indefinite volume no very accurate estimate of the molar concentration could be made.

### Summary

1. We have shown that in water solution at the lowest temperatures investigated an equilibrium exists among maleic, malic and fumaric acids.

2. At the higher temperatures maleic acid substantially disappears and the equilibrium is between fumaric acid and inactive malic acid.

3. At the higher temperatures approximately the same end-point is reached whether one starts with maleic, fumaric, inactive malic or *levo*-malic acid.

4. An analytical method is described for the detection of small amounts of maleic acid in mixtures with fumaric and malic acid.

5. Malic acid solutions are practically unchanged by simple boiling at atmospheric pressure.

6. Malic acid does not appear to be necessarily an intermediate product in the transformation of maleic to fumaric acid.

7. An exact study of the equilibrium conditions among these acids would be of great scientific interest. We have pointed out certain manipulative and analytical difficulties which would have to be overcome before such accurate determinations could be made.

NEW YORK, N. Y.



group of the second molecule. This reaction corresponds to that which takes place when phenols or naphthols react with benzaldehyde. Phenols or naphthols do not react with benzaldehyde unless a mineral acid is used and then the reaction proceeds readily, with or without a solvent such as glacial acetic acid.<sup>11</sup> Ordinarily, triphenylmethane derivatives are obtained, but Claisen<sup>12</sup> has shown that, by working at low temperatures, the acetals from certain of the phenols and naphthols could be isolated as intermediate products. Whereas ordinary phenol-benzaldehyde acetals tend chiefly to rearrange to triphenylmethane compounds, this salicyl aldehyde hemi-acetal of salicyl aldehyde has a tendency to condense as shown in Steps III and IV, which involve, respectively, acetal formation and dehydration to form disalicyl aldehyde.

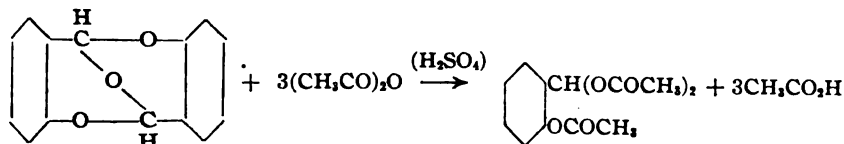
If this explanation is correct, it may be understood why various acid chlorides cause the reaction to take place. A small amount of acid chloride reacts first with the hydroxyl of the salicyl aldehyde, giving hydrochloric acid. This mineral acid being the catalyst usually used for the formation of an acetal causes Steps II and III to occur. The remaining portion of the acid chloride now acts as a dehydrating agent to remove water and thus gives Step IV. This deduction leads to the conclusion that any very small amount of mineral acid in the presence of a dehydrating agent should cause this reaction to take place. Experiments fully substantiated this. Salicyl aldehyde is unaffected by cold acetic anhydride even after long standing. If to this mixture, however, a small drop of conc. sulfuric acid is added, an immediate reaction takes place. The mixture turns red and heat is evolved sufficient to boil the acetic anhydride, if it is not cooled. Inside of 3 minutes after the sudden reaction is over, disalicyl aldehyde separates from the cooled reaction mixture in yields which amount to more than 85% of those calculated. In place of sulfuric acid, phosphoric acid or hydrochloric acid may be used.

Acids are catalyzers for the decomposition as well as for the formation of acetals. Treatment of disalicyl aldehyde with conc. sulfuric acid to yield salicyl aldehyde has already been mentioned. Warming with strong acid is rather drastic treatment, however. A very simple experiment showing the decomposition of disalicyl aldehyde with acids consists in treating pure disalicyl aldehyde with an excess of acetic anhydride. No reaction takes place, even on long boiling. When, however, a drop of sulfuric acid is added to the cold solution and the mixture allowed to remain at room temperature, large, heavy transparent crystals separate from the solution within 24 hours. These crystals are salicyl aldehyde triacetate.

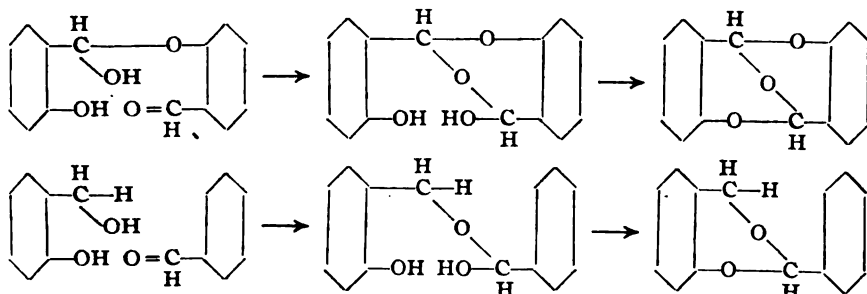
If Steps III and IV described above are correct, it should be possible to form with ease a compound of properties similar to disalicyl aldehyde by

<sup>11</sup> Russanow, *Ber.*, **22**, 1944 (1889). Michael, *Am. Chem. J.*, **9**, 130 (1886).

<sup>12</sup> Claisen, *Ann.*, **237**, 269 (1887).



the condensation of saligenin with benzaldehyde. The analogy is best shown by the following two equations.

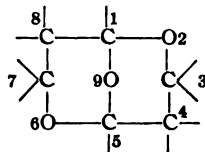


It is true that the hydroxyl group in the saligenin is an alcohol group, while that in the intermediate step of the formation of disalicyl aldehyde is a hemi-acetal hydroxyl; nevertheless the reactions should proceed in a somewhat similar manner. The experiments came up to expectations. The reaction between saligenin and benzaldehyde does take place with the greatest ease and does give a compound which is exactly analogous to disalicyl aldehyde in properties. In fact, the reaction takes place so readily that it is merely necessary to warm these two substances together in the presence of a very small amount of acid without the use of a solvent or dehydrating agent. To get the best results in forming disalicyl aldehyde, a high temperature must be avoided; likewise a high temperature must be avoided in the formation of this new product. The compound forms with such ease that even benzoic acid acts as a catalyst and in fact it is preferable to use this, rather than hydrochloric acid, since the latter tends to cause saligenin to condense with itself to a certain extent, thus lowering the yield of desired product.

This new condensation product of saligenin and benzaldehyde is 2-phenyl-1,3-benzodioxan or phenyl-methylene saligenin. It is a well crystallized compound, unreacted upon by hydroxyl or carbonyl group reagents, insoluble in and extremely stable to alkalis. It dissolves in warm conc. sulfuric acid to give a red solution which, on dilution, yields benzaldehyde and a resinous substance, presumably a saligenin condensation product. The compound decomposes in a manner similar to that of disalicyl aldehyde when dissolved in acetic anhydride and treated with a drop of sulfuric acid. Benzylidene di-acetate is readily obtained, together with a saligenin resin.

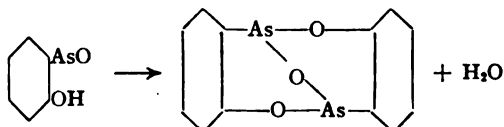
The reaction represented by the condensation of saligenin and benzaldehyde to give a benzo-dioxan is not a limited one. It has already been shown that other aldehydes react in the same way with saligenin and an investigation as to the scope of this reaction is now under way.

The structure represented by disalicyl aldehyde involves a new type of nucleus and consequently it is necessary to outline a convenient system of nomenclature. The following formula represents the nucleus and numbered as in the figure should be called a 2,6,9 bis-dioxan.



By using this system of nomenclature, disalicyl aldehyde is then dibenzo-2,6,9-bis-dioxan.

A compound which is probably of analogous structure to disalicyl aldehyde is formed when *o*-amino arsine oxide is diazotized in dilute aqueous solution and the diazo compound treated with sulfurous acid. Two molecules of the intermediate *o*-hydroxy-*γ*-arsine oxide, which is very similar in constitution to salicyl aldehyde, lose a molecule of water spontaneously and form the anhydride, a substance which the writer designates as *o*-hydroxy-phenyl-arsinoxide anhydride.<sup>13</sup>



The formation of such a compound as disalicyl aldehyde from salicyl aldehyde is of more than ordinary interest because of the fact that aliphatic  $\beta$ -hydroxy aldehydes should resemble salicyl aldehyde in their reactions. The former substances should, therefore, be expected to form bis-dioxans, and preliminary experimental evidence leads to the conclusion that such is the case. Since the monosaccharides are  $\beta$ -hydroxy aldehydes, it is possible that some of the complex condensation products of the monosaccharides contain this bis-dioxan grouping.

### Experimental Part

**Preparation of Disalicyl Aldehyde (dibenzo-2,6,9-bis-dioxan).—**Thirty g. (1 mole) of salicyl aldehyde and 25 g. (1 mole) of acetic anhydride are mixed and cooled to 0° in an ice-and-salt mixture. One drop of conc. sulfuric acid is added and the mixture immediately stirred to make it homogeneous. Within 10 seconds a deep cherry-red color has developed and a vigorous reaction takes place which is complete within 2 or 3 minutes, after which time the mixture practically solidifies. The mass is stirred thoroughly in

<sup>13</sup> Kalb, *Ann.*, 423, 70 (1921).

order to be sure that all of the salicyl aldehyde has reacted, and it is best to allow the mixture to stand in the ice for 5 or 10 minutes longer. By filtration with suction and washing with water, then drying, 24 g. of disalicyl aldehyde is obtained which corresponds to over 85% of the calculated amount. There is a small additional amount of product formed by allowing the filtrate from the crystals to stand in ice for 10 to 15 minutes longer.

The product is best purified by recrystallization from alcohol, from which it forms white, prismatic needles melting at 130° (corr.). The melting points previously reported in the literature vary from 127° to 130°.

If a larger amount of acetic anhydride is used, the reaction takes place in essentially the same way but not so good a yield results. It is also necessary to take certain precautions in using larger amounts of acetic anhydride; the mixture should not be allowed to stand too long before filtering the disalicyl aldehyde since the latter reacts with acetic anhydride in the presence of acid to form salicyl aldehyde tri-acetate. With the smaller amount of acetic anhydride, the product precipitates so quickly that there is no need for longer standing.

If the reaction mixture is not very carefully controlled in an ice and salt bath, the heat evolved is so great that the mixture will boil, and on cooling it, a poorer yield of disalicyl aldehyde is obtained.

In place of conc. sulfuric acid, a drop of glacial phosphoric acid may be used. Hydrochloric acid is also a catalyst but it is necessary to alter the procedure slightly. One-half of the acetic anhydride is saturated with dry hydrogen chloride. This saturated solution is then added to the mixture of salicyl aldehyde and the other half of the acetic anhydride at room temperature. The reaction develops heat, but not so much as in the case of the other acids. A somewhat longer time is required for the precipitation of the disalicyl aldehyde and the yields are not quite so high.

Trichloro-acetic acid may also be used as a catalyst but the results are still poorer than in the cases already mentioned.

**Conversion of Disalicyl Aldehyde to Salicyl Aldehyde Tri-acetate.**—Five g. (1 mole) of disalicyl aldehyde is dissolved in 14 g. (6 moles) of acetic anhydride, and one drop of conc. sulfuric acid is added. This mixture is allowed to stand at room temperature for a day or two. The tri-acetate of salicyl aldehyde separates in large, heavy crystals of rhombic form, some of which are 6 to 12 mm. on a side. They melt at 100–101° and do not lower the melting point of salicyl aldehyde tri-acetate (m. p. 100–101°) prepared according to the method of Barbier.<sup>14</sup>

**Preparation of 2-Phenyl-1,3-Benzo-dioxan (Phenylmethylene Saligenin).**—Ten g. (1.1 mole) of saligenin and 10 g. (1 mole) of benzaldehyde which has previously been saturated with benzoic acid, are heated for 2 hours on a steam cone. A light yellow resinous looking product results. The reaction mixture, after standing at room temperature for 2 hours, is treated with 300 cc. of a 5% sodium hydroxide solution and cooled in ice so that the product will solidify. The white solid is filtered and washed with water. It is crude 2-phenyl-1,3-benzo-dioxan and corresponds to practically a quantitative yield of product. It is best purified by dissolving 3 g. in 70 cc. of 95% alcohol, adding 30 cc. of water, warming this solution until it is clear and then allowing it to stand in an open beaker at room temperature. Within half an hour a white crystalline precipitate forms. After two crystallizations, pure material is produced, melting at 54°.

A drop of conc. hydrochloric acid may be used as a catalyst in place of the benzoic acid. It is then necessary merely to heat the reaction mixture of saligenin, benzaldehyde and a drop of hydrochloric acid until solution takes place. The mixture is allowed to stand for several hours at room temperature. The product is isolated in the same man-

<sup>14</sup> Barbier, *Bull. soc. chim.*, [2] 33, 53 (1880).

ner as described above, but the yields are not so good as with the benzoic acid method. If the reaction mixture, when hydrochloric acid is used, is heated longer, the yields are in general still poorer, due probably to a partial resinification of the saligenin.

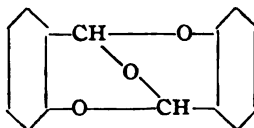
*Analyses.* Subs. 0.1342:  $\text{CO}_2$ , 0.3885;  $\text{H}_2\text{O}$ , 0.0715. Subs. 0.5957, 0.4810:  $\text{C}_6\text{H}_6$ , 43.9, 43.9;  $\Delta T_F$ , 0.319°, 0.257°. Calc. for  $\text{C}_{14}\text{H}_{12}\text{O}_2$ : C, 79.24; H, 5.66; mol. wt., 212. Found: C, 78.97; H, 5.92; mol. wt., 212, 213.

2-Phenyl-1,3-benzo-dioxan is soluble in all the common organic solvents. It does not dissolve in solutions of alkali and is unchanged even after long boiling with 20% sodium hydroxide solution. When treated with conc. sulfuric acid, an immediate decomposition takes place with the formation of benzaldehyde and red lumps of resinified saligenin. The product gives no aldehyde or ketone test with sodium hydrogen sulfite, phenylhydrazine or hydroxylamine; it gives no test with hydroxyl group reagents such as ferric chloride or acetic anhydride even after long boiling.

**Conversion of 2-Phenyl-1,3-benzo-dioxan to Benzylidene Diacetate and Saligenin Resin.**—Ten g. (1 mole) of 2-phenyl-1,3-benzo-dioxan is mixed with 30 g. (6 moles) of acetic anhydride and one drop of conc. sulfuric acid at room temperature. The mixture is then allowed to stand for several days. At the end of this time the acetic anhydride is distilled *in vacuo*, the residue taken up in ether, washed with water and then with a dilute solution of sodium carbonate. The ether solution is then dried over anhydrous sodium sulfate, the ether distilled, then the residue distilled *in vacuo*. A constant boiling, colorless fraction comes over at 125° at 4 mm. pressure which on cooling and inoculating with a crystal of benzylidene diacetate almost completely solidifies. The melting point is 45°, which agrees with that found in the literature for benzylidene diacetate. The residue in the distilling flask consists of a pale yellow, heavy oil which does not distil at 250° at 4 mm. pressure and at ordinary temperatures forms a resin-like mass which is without question a saligenin resin.

### Summary

1. Disalicyl aldehyde has been shown to have the following formula



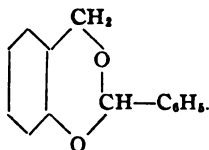
and may be called dibenzo-2,6,9-bis-dioxan. The formula accounts for all of the known properties of this substance.

2. A possible mechanism for the formation of such a structure from salicyl aldehyde is given and from this mechanism conclusions have been drawn as to new methods by which it should be possible to prepare disalicyl from salicyl aldehyde.

3. Disalicyl aldehyde may be formed almost quantitatively by the action of a drop of mineral acid upon a solution of salicyl aldehyde in acetic anhydride.

4. It was concluded from the mechanism of the formation of disalicyl aldehyde that a compound should form from saligenin and benzaldehyde which should possess similar properties to disalicyl aldehyde. This substance does form and may be looked upon as 2-phenyl-1,3-benzo-dioxan,

or phenylmethylene saligenin, forming white plates with a melting point of  $54^{\circ}$  and having the structure



URBANA, ILLINOIS

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF THE UNIVERSITY OF QUEENSLAND]

## RACEMIC ACID IN SOLUTION

BY STUART WORTLEY PENNYCUICK

Received December 30, 1921

Several physical methods have been used to show the existence (or nonexistence) of the racemic molecule in solution. Some have given positive results, while others point to its complete breakdown into the two active forms.

Bruni and Padoa<sup>1</sup> from molecular-weight determinations conclude that racemic acid exists in solution in the presence of excess of one of the active forms. Kuster<sup>2</sup> by solubility determinations, and Dunstan and Thole<sup>3</sup> by a viscosity method find positive results. Stewart<sup>4</sup> by absorption spectra observations, and Rankin and Taylor<sup>5</sup> also find evidence of its existence. On the other hand specific gravity and heat of neutralization determinations,<sup>6</sup> as well as a rotatory dispersion method,<sup>7</sup> show no evidence of its independent existence.

An interfacial tension method as described in this paper leaves little doubt that the racemic molecule does exist in solution.

The interfacial tensions between aqueous solutions of (a) *dextro* tartaric, (b) *levo* tartaric, (c) racemic acid, and an inert liquid have been measured and the results compared. As a comparison of the interfacial tensions was aimed at, the drop method as developed by Tate,<sup>8</sup> Morgan<sup>9</sup> and co-workers, and Lohnstein<sup>10</sup> was adopted. The apparatus used was as

<sup>1</sup> Bruni and Padoa, *Atti accad. Lincei.*, **11**, 212 (1902).

<sup>2</sup> Kuster, *Ber.*, **31**, 1847 (1898).

<sup>3</sup> Dunstan and Thole, *J. Chem. Soc.*, **93**, 1815 (1908).

<sup>4</sup> Stewart, *ibid.*, **91**, 1537 (1907).

<sup>5</sup> Rankin and Taylor, *Proc. Roy. Soc. Edinburgh*, **27**, 172 (1907).

<sup>6</sup> Jahn, *Wied. Ann.*, **43**, 306 (1891).

<sup>7</sup> Darmais, *Trans. Faraday Soc.*, **10**, 80 (1914).

<sup>8</sup> Tate, *Phil. Mag.*, [iv] **27**, 176 (1864).

<sup>9</sup> Morgan, *THIS JOURNAL*, **30**, 360 (1908).

<sup>10</sup> Lohnstein, *Z. physik. Chem.*, **64**, 686 (1908).

described by Lewis.<sup>11</sup> The interfacial tension,  $\pi$ , is taken as proportional to the weight of a drop, *i. e.*,

$$\pi = K \times \text{wt. of 1 drop} = \frac{K V \text{ density}}{n}$$

where  $n$  is the number of drops for a given volume  $V$ . As the same volume is used in each case, and solutions of corresponding densities are taken,  $\pi \sim 1/n$ . It is therefore sufficient to read the drop number for fixed volumes, and plot it against the concentrations.

Chemically pure *dextro* tartaric acid was recrystallized. Some of it was converted into the racemic acid and the product recrystallized thrice. *Levo* tartaric acid was then made from racemic acid through the cinchonine salt, and recrystallized until its rotation gave the maximum value. Thirty per cent. solutions of the *dextro* and *levo* acids were made up and a 15% solution of the racemic acid. Corresponding diluted solutions were used, and the drop number given by toluene and by paraffin obtained. The absence of reaction between the oil and the acid was shown by comparing the drop number given by the oil after shaking with the acid, with the drop number given by the untreated oil. No change was observed.

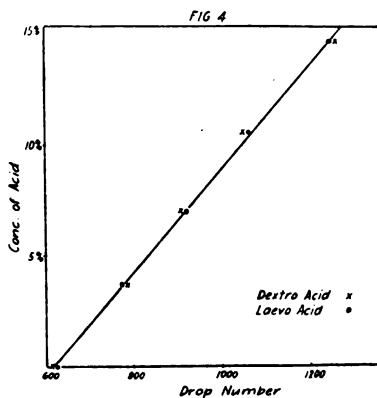
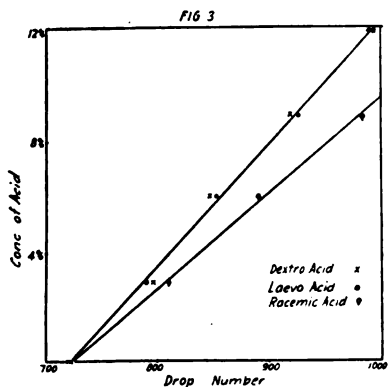
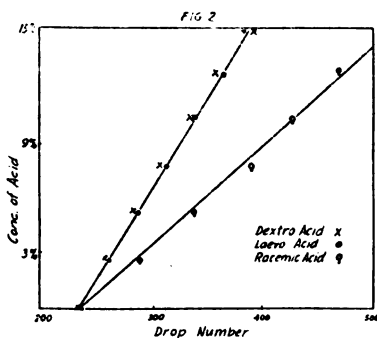
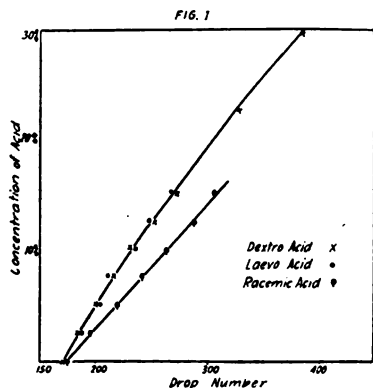
TABLE I

DROP NUMBER AGAINST TOLUENE				DROP NUMBER AGAINST PARAFFIN		
Concentration of acid %	<i>Dextro</i> acid	<i>Levo</i> acid	Racemic acid	<i>Dextro</i> acid	<i>Levo</i> acid	Racemic acid
..	171	173	172	233	235	233
2.5	183	186	195	260	257	289
5	200	204	220	286	285	338
7.5	216	211	242	310	314	390
10	233	234	264	339	338	427
12.5	253	251	288	359	366	470
15	274	271	308	394	385	522
22.5	330	...	...	...	...	...
30	386	...	...	...	...	...

If the interfacial tension of such solutions be measured against an optically active liquid an interesting question arises. Certain optically active solutions of enzymes have a marked selective action on enantiomorphs, attacking one form strongly and the other form very slightly. Numerous glucosides are selectively hydrolyzed in this way; *e. g.*,  $\alpha$ -methyl glucoside and  $\alpha$ -methyl galactoside by maltase and not by emulsin, while the enantiomorphs are hydrolyzed by emulsin and not by maltase. Bayliss has shown that in nearly every case examined both forms are actually attacked. No satisfactory physical or chemical explanation has been put forward for this selective action, and neither a vitalistic theory nor a "lock and

<sup>11</sup> Lewis, *Phil. Mag.*, 1908.

key" explanation goes very far. The suggestion has been put forward by Dr. Denham (and in fact it was this suggestion that started the present work) that the selective action might be due to selective adsorption of the optically active substrate upon the surface of the optically active catalyst. Evidence concerning such selective adsorption might possibly be afforded by determining the interfacial tensions of optically active solutions against an optically active oil, or against an oil rendered optically active by such a solute as camphor. The difficulty



of procuring in sufficient quantity an oil which possessed at the same time the desired degree of optical activity and yet did not dissolve in, nor react chemically with, the aqueous solution of the chosen active solute, compelled the author to use as the active oil a solution of camphor in benzene. The absence of reaction between this active oil and the aqueous solution of the active acid was again tested by taking the drop number of this oil before and after shaking with an aqueous solution of *d*-tartaric acid. The values recorded were identical.

Drop numbers of the *dextro*, *levo* tartaric and racemic acids were then



taken against the camphor-benzene solution,<sup>12</sup> and also those of *dextro* and *levo* camphor-sulfonic acids against the camphor-benzene solution.

TABLE II

DROP NUMBER AGAINST A SOLUTION OF CAMPHOR IN BENZENE

Conc. of acid <i>d</i> -Tartaric <i>l</i> -Tartaric Racemic			Conc. of acid <i>d</i> -Camphor- <i>l</i> -Camphor-			
in water			sulfonic acid sulfonic acid			
%	17%			%	26%	
..	720	724	728	..	613	619
3	796	791	810	3.7	795	777
6	846	852	891	7	915	916
9	920	925	983	10.5	1056	1059
10.4	...	...	1015	14.7	1257	1253
12	994	990	..	..	..	..

### Conclusion

The results show that there is no measurable difference in interfacial tension, against the several liquids, between the *dextro* and the *levo* substances chosen, indicating that there is no selective absorption of such enantiomorphs, which are remarkable for their similarity of physical properties.

The divergence of the curve for either of the active tartaric acids from that for the racemic acid (see Figs. 1, 2 and 3) appears to admit of only one explanation, the existence in solution of the racemic acid molecule. As the dilution increases, the curves indicate an increasing "dissociation" of the racemic acid into the *d* and *l* forms.

I am indebted to Professor H. G. Denham, now of the University of Cape Town, South Africa, for his initial suggestion and for his advice during the progress of this work.

[CONTRIBUTION FROM THE KENT CHEMICAL LABORATORY OF THE UNIVERSITY OF CHICAGO]

## C<sub>18</sub> FATTY ACIDS. IV. A REARRANGEMENT OF THE BENZILIC ACID TYPE IN THE ALIPHATIC SERIES

BY BEN H. NICOLET AND ALFRED E. JURIST<sup>1</sup>

Received January 2, 1922

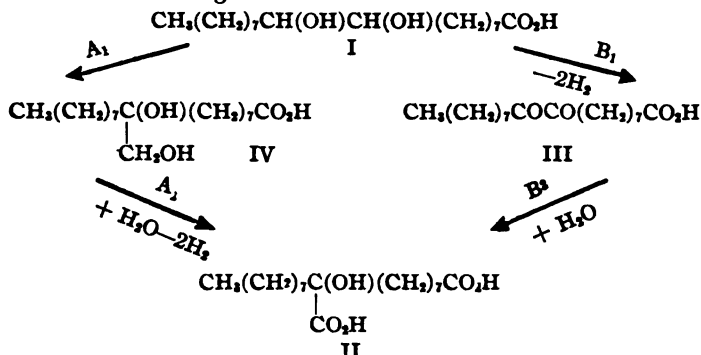
Some time ago Le Sueur<sup>2</sup> described the fusion of 9,10-dihydroxystearic acid (I) with potassium hydroxide. The principal reaction was shown to be the formation of  $\alpha$ -hydroxy- $\alpha$ -octyl-sebacic acid (II), resembling benzilic acid in structure, and the evolution of hydrogen, though the considerable amount of material not accounted for indicated that side reactions were also taking place.

<sup>12</sup> The author is indebted to Professor Read, University of Sydney, for the supply of camphor-sulfonic acids.

<sup>1</sup> The material here presented was used by Alfred E. Jurist in partial fulfilment of the requirements for the degree of Doctor of Philosophy in the University of Chicago.

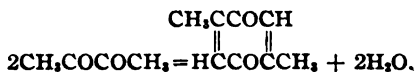
<sup>2</sup> Le Sueur, *J. Chem. Soc.*, 79, 1313 (1901).

Apparently, these results might have been reached in either of two ways, as shown in the following chart.



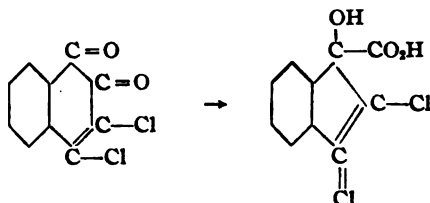
The reaction scheme designated as  $\text{A}_1$  and  $\text{A}_2$  has little to commend it. The reaction  $\text{A}_2$  is perfectly normal, but  $\text{A}_1$  has, to the writer's knowledge, no strong resemblance to any known type of rearrangement. No product corresponding to the glycol (IV) has been isolated from the products formed, either by us or by Le Sueur, and the assumption of such a course of reaction is accordingly purely hypothetical. Formally, Reactions  $\text{B}_1$  and  $\text{B}_2$  appear more likely to represent the reaction correctly. The oxidation represented by  $\text{B}_1$  is perfectly normal, and  $\text{B}_2$  represents a typical benzilic acid rearrangement.

Von Pechmann<sup>3</sup> attempted in vain to obtain a rearrangement of this type by fusion of "diacetyl" or of "acetylpropionyl" with alcoholic potash. Instead, quinones were formed.



From this result, von Pechmann draws the rather sweeping conclusion that aliphatic  $\alpha$ -diketones which do *not* give this reaction, will undergo the benzilic acid rearrangement. Considering that no cases of the latter type were investigated by him, the conclusion seems unduly far-reaching.

There remains, on the other hand, very little doubt that this rearrangement occurs much more generally than has usually been recognized, as shown, for example, by the following reaction described by Zincke.<sup>4</sup>



<sup>3</sup> Von Pechmann, *Ber.*, 21, 1411 (1888).

<sup>4</sup> Zincke, *ibid.*, 19, 2500 (1886); 20, 1265, 2053, 2890 (1887).

Furthermore, Nef<sup>5</sup> in his extensive work on saccharinic acids explained their formation on the basis of this rearrangement, and his pupil Evans<sup>6</sup> considered a similar rearrangement obvious in the case of diketosuccinic acid. Finally, Lachman<sup>7</sup> has, since the completion of the present investigation, discussed the very similar case of dihydroxy-tartaric acid from this point of view.

It is then evident that aliphatic compounds may, and sometimes do, undergo the benzilic acid rearrangement. An analysis of the work quoted above shows, however, that in none of the cases mentioned has the compound undergoing rearrangement had the structure  $RCH_2COCOCH_2R'$ ; in other words, the absence of two hydrogens attached to each of the carbons adjoining each of the keto groups, has prevented interference by the reaction described by von Pechmann.

The present work was undertaken to show whether diketostearic acid (III) could be considered as an intermediate product in Le Sueur's reaction.

This acid (III) has been prepared by Overbeck<sup>8</sup> by the oxidation of stearolic acid with nitric acid. A somewhat more convenient method involving the oxidation of dihydroxy-stearic acid with chromic acid, was developed. The diketo acid so obtained was fused with caustic potash at 160°, 190° and 225°. Only at the lowest temperature could dihydroxy-stearic acid (I) and hydroxy-octyl-sebacic acid (II) be isolated, so that the reactions at higher temperatures were not further studied. Azelaic and pelargonic acids were also obtained.

As hydrogen is not evolved in the action of potassium hydroxide on diketostearic acid (cf. also Reaction B<sub>2</sub>), the formation of dihydroxy-stearic acid can be readily explained only on the ground of an intermolecular oxidation and reduction, which would be quite similar to the well known Cannizzaro Reaction<sup>9</sup> of aromatic aldehydes. By analogy, one might expect the formation, for each mol. of dihydroxy acid, of 2 mols. of pelargonic acid and 2 mols of azelaic acid. It is worthy of note that no diketostearic acid is recoverable after the fusion, and that a *reduction product*, the dihydroxy acid, is formed on heating it with potassium hydroxide, a reaction usually associated with oxidation.

From the considerations advanced above, each gram of the dihydroxy acid formed should involve the formation of 1.19 g. of azelaic acid and 1.0 g. of pelargonic acid. These acids were isolated in quantities of 0.36 g. and 0.54 g., respectively, which, considering the properties of the acids

<sup>5</sup> Nef, *Ann.*, **357**, 306, 308 (1907) and elsewhere.

<sup>6</sup> Evans, *Am. Chem. J.*, **35**, 116 (1906).

<sup>7</sup> Lachman, *THIS JOURNAL*, **43**, 2092 (1921).

<sup>8</sup> Overbeck, *Ann.*, **140**, 63 (1866).

<sup>9</sup> Cannizzaro, *ibid.*, **88**, 129 (1853).

in question and the methods available for their isolation, are considered to be in satisfactory relation with the requirements mentioned above.

In addition, the fusion at  $160^{\circ}$  yielded  $\alpha$ -hydroxy- $\alpha$ -octyl-sebacic acid (II), which was sufficiently identified with Le Sueur's product. This is interpreted to mean that the diketo acid has undergone a rearrangement of the benzilic acid type, as indicated by Reaction B<sub>2</sub>. Simultaneously, intermolecular oxidation and reduction yielded dihydroxy-stearic acid, pelargonic acid, and azelaic acid. As much of the original material was unaccounted for, and products were obtained which could not be distilled even under very greatly reduced pressure, the formation of a complex quinone according to von Pechmann is not excluded.

The fact that dihydroxy-stearic acid is obtained in this reaction makes it at least conceivable that the presence of the acid (II) might be explained by the intermediate formation of the dihydroxy acid. This is doubted for the following reasons: (1) dihydroxy-stearic acid, heated with potassium hydroxide at temperatures of  $160^{\circ}$  or  $190^{\circ}$ , was recovered almost quantitatively unaltered; (2) the concentration of the dihydroxy acid formed in these reactions is relatively small.

Consequently it is considered that diketostearic acid is an intermediate product in Le Sueur's reaction. The relatively small yield (11.86%) of acid (II) here recorded, may be explained on the following grounds: (1) the relatively large concentration of dihydroxy-stearic acid under the conditions used by Le Sueur would tend to prevent the formation of pelargonic and azelaic acids; (2) the hydrogen evolved under Le Sueur's conditions (but not in the case here described) would tend likewise to prevent this loss; (3) condensation of the diketo acid to form quinone derivatives, according to von Pechmann (suspected, but not actually demonstrated) is a reaction bimolecular with respect to the diketo acid, and its rate is accordingly proportional to the square of the latter's concentration. It therefore makes an enormous difference whether this acid is the starting material, or merely an intermediate product in the reaction.

### Experimental Part

The necessary dihydroxy-stearic acid was prepared essentially according to Saytzeff,<sup>10</sup> except that it was found more convenient to dissolve all of the manganese dioxide formed by treatment with sulfite and an excess of sulfuric acid, thus avoiding a somewhat difficult filtration. The yield of material was 40%, m. p.  $131.5^{\circ}$ .

**Preparation of 9,10-Diketostearic Acid.**—Twenty g. of dihydroxy-stearic acid was dissolved in 1200 cc. of glacial acetic acid. This solution was kept at  $20^{\circ}$ , and stirred while a solution of 12 g. of chromic anhydride in 400 cc. of acetic acid, containing 2 cc. of conc. sulfuric acid was added gradually. Within 20 minutes the solution became blue-green; the reaction was then stopped by pouring the mixture into 1.5 liters of water. The precipitated diketostearic acid was removed by filtration, washed, dried in a vacuum and recrystallized from alcohol and from ether (dihydroxy-stearic acid is very insoluble

<sup>10</sup> Saytzeff, *J. prakt. Chem.*, [2] 33, 304 (1886).

in ether). The yield of material was 25% m. p.  $86^{\circ}$ . The product was analyzed by titration.

Calc. for  $C_{18}H_{32}O_4$ : Equiv. wt., 312.0. Found: 310.6, 311.7.

Several other methods were tried in the hope of improving the yield. Dilution of the acetic acid with acetone, and oxidation with barium peroxide, manganese dioxide, or permanganate in acid solution, all gave less satisfactory results. Oxidation, under the conditions described above, of esters of dihydroxy-stearic acid, gave good, but not better, results.

**Methyl 9,10-Diketostearate.**—This was prepared from methyl dihydroxy-stearate, by a method similar to that used for the acid. The ester was obtained in 25% yield, m. p.  $55^{\circ}$ .

*Analyses.* Calc. for  $C_{19}H_{34}O_4$ : C, 69.94; H, 10.43; O, 19.63. Found: C, 69.86, 69.90; H, 10.63, 10.67; O, 19.51, 19.41.

**Ethyl 9,10-Diketostearate.**—Similarly, this was obtained in 15% yield as yellow needles, m. p.  $50^{\circ}$ .

*Analyses.* Calc. for  $C_{20}H_{36}O_4$ : C, 70.59; H, 10.59; O, 18.82. Found: C, 70.40, 70.54; H, 10.90, 10.63; O, 18.70, 18.73.

**Fusion of Diketostearic Acid with Potassium Hydroxide at  $160^{\circ}$ .**—Thirteen g. of 9,10-diketostearic acid was fused for 5 minutes at  $160^{\circ}$  with 65 g. of potassium hydroxide, moistened with sufficient water. The fused mass was then poured into water and acidified with dil. sulfuric acid. After standing overnight the mixture was filtered and the filtrate extracted thrice with ether. After removing the ether and recrystallizing the solid from hot water, the extracted material weighed 0.4 g. and melted at  $106^{\circ}$ . The equivalent weight was determined by titrating with alcoholic potash.

Calc. for azelaic acid,  $C_9H_{16}O_4$ : Equiv. wt., 94.0. Found: 93.95, 94.05.

The solid obtained above was extracted with chloroform. On standing overnight, the extract deposited crystals which, purified from hot alcohol, melted at  $131.5^{\circ}$  and weighed 0.9 g. Analysis proved that this was dihydroxy-stearic acid, though special precautions had been taken to see that the original diketo acid had been separated completely from this substance.

*Analyses.* Calc. for  $C_{18}H_{32}O_4$ : C, 68.35; H, 11.39; O, 20.25. Found: C, 68.06, 68.17; H, 11.65, 11.52; O, 20.29, 20.31.

The remaining chloroform solution was distilled with steam until no more oil came over. The distillate was made alkaline, concentrated to a small volume, acidified, and extracted with ether. The oil thus recovered weighed 0.6 g., and had the odor of pelargonic acid.

Calc. for pelargonic acid,  $C_9H_{18}O_2$ : Equiv. wt., 158. Found: 157.9.

The residue from this steam distillation was filtered hot and the filtrate made alkaline, concentrated to a small volume, acidified, and extracted with ether. This extract yielded only 0.4 g. of an oil which was not further identified.

The semi-solid oily material remaining on the filter in the operation described above, was dissolved in ether. After removing the ether the residue was spread on a porous plate and placed in a steam oven. There remained 1.6 g. of a somewhat grayish solid, which, after further purification, melted at  $110^{\circ}$ , either alone, or after mixing with hydroxy-octyl-sebacic acid obtained by Le Sueur's method. Its identity was further proved by analysis.

*Analyses.* Calc. for  $C_{18}H_{34}O_6$ : C, 65.45; H, 10.30; O, 24.24. Found: C, 65.20; H, 10.59; O, 24.21.

Calc. for  $C_{18}H_{34}O_6$ : Equiv. wt., 330.0. Found: 328.2.

**Fusion at Higher Temperatures.**—Fusions for 5 minutes, similar to that just described, were performed at 190° and at 225°. In neither case was it found possible to isolate either dihydroxy-stearic acid, or hydroxy-octyl-sebacic acid.

**Fusion of Dihydroxy-stearic Acid with Potassium Hydroxide.**—The fusion was made in exactly the same way as described above for the fusion of diketostearic acid. At 160°, it was found possible to recover (pure) 90% of the original dihydroxy acid. No hydroxy-octyl-sebacic acid could be found. At 180°, the results were the same, 93% of the original acid being recovered.

### Summary

1. The formation of  $\alpha$ -hydroxy- $\alpha$ -octyl-sebacic acid in the alkaline fusion of dihydroxy-stearic acid, as observed by Le Sueur, is probably the first recognized "benzilic acid" rearrangement of a compound of the type  $RCH_2COCOCH_2R'$ , proceeding through diketostearic acid as an intermediate product.

2. This same product is formed when diketostearic acid is fused with alkali at 160°.

3. In this same fusion (2) dihydroxy-stearic acid is formed, along with pelargonic and azelaic acids, in a modified Cannizzaro reaction.

CHICAGO, ILLINOIS

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[CONTRIBUTION NO. 11 FROM THE DEPARTMENT OF CHEMICAL RESEARCH, PARKE, DAVIS AND COMPANY]

### ALKYLBENZYL BARBITURIC ACIDS

BY ARTHUR W. DOX AND LESTER YODER

Received January 26, 1922

Notwithstanding the great number of dialkyl and alkyl-aryl barbituric acids that have been prepared and described since Emil Fischer's discovery of the hypnotic properties of veronal (diethyl barbituric acid), little attention has been given the alkylbenzyl derivatives. The fact has been repeatedly demonstrated that the presence of two hydrocarbon radicals on the 5-carbon atom is necessary to confer sleep-producing properties upon barbituric acid. The two radicals may or may not be identical, but one alone is not sufficient to give any marked physiological action.

In view of the recent work of Macht<sup>1</sup> and others on the antispasmodic effect of benzyl derivatives, notably benzyl alcohol and its esters, the possibility suggested itself that a barbituric acid derivative with combined hypnotic and antispasmodic properties might be prepared by substituting a benzyl group for one of the alkyls in the derivatives of the veronal series. The benzyl would then play the role of an alkyl radical in stabilizing the molecule and thus confer hypnotic properties within the limits of the "distribution coefficient," or ratio of solubility in fat to solubility in water, and at the same time contribute its specific antispasmodic "benzyl effect."

<sup>1</sup> Macht, *J. Pharmacol.*, 11, 176 (1918).

In a homologous series with increasing fat solubility and decreasing water solubility it should be possible to find one derivative with the distribution coefficient required by the Overton-Meyer hypothesis. In this regard we were successful, for the benzylethyl derivative showed marked hypnotic properties. However, the specific effect of the benzyl group was quite at variance with our predictions. Instead of an antispasmodic effect the result was quite the opposite. When the dose administered, approached the toxic dose, a condition of tetanus resulted. The physiological experiments on mice and dogs were performed by other workers in this laboratory and will be discussed in detail elsewhere.

Of the many possible alkylbenzyl barbituric acids, only three have thus far been described. The allylbenzyl derivative was prepared by Johnson and Hill<sup>2</sup> from ethyl allylbenzyl malonate, urea and sodium ethylate. Isopropylbenzyl and cyclohexylbenzyl barbituric acids, prepared by condensing the corresponding di-substituted cyano-acetic esters with guanidine and hydrolyzing the resulting di-imino-pyrimidines, are described in a Bayer patent.<sup>3</sup> Arylbenzyl derivatives known are dibenzyl<sup>4</sup> and phenylbenzyl<sup>5</sup> barbituric acid.

To any one familiar with the properties of hypnotics of the veronal series, it will be apparent that three of the above, namely dibenzyl, phenylbenzyl and cyclohexylbenzyl, on account of the size of the substituent groups, would be too insoluble in water to exert any marked hypnotic action when administered by mouth. Regarding the other two, allylbenzyl and isopropylbenzyl, no physiological data are available. Of these true alkylbenzyl derivatives one contains an unsaturated alkyl and the other a secondary alkyl radical. Our purpose was to prepare a series of alkylbenzyl barbituric acids, with alkyl radical derived from the primary aliphatic alcohols. No such derivatives have thus far been described.

In the preparation of these alkylbenzyl barbituric acids we employed the method introduced by Fischer and Dilthey, and subsequently adopted by many other investigators. Briefly, it consists in heating an ethyl dialkylmalonate with urea and an excess of sodium ethylate in an autoclave. The desired alkyl groups are introduced into the ethyl malonate. Direct substitution in barbituric acid is not feasible except in the case of the very reactive alkyl halides, such as allyl bromide. We found, however, that the benzyl group may be introduced directly into barbituric acid or a mono-alkyl barbituric acid, though the yield is not satisfactory.

In the series of ethyl alkylbenzylmalonates which we prepared the only one previously described is the methyl derivative. This was prepared

<sup>2</sup> Johnson and Hill, *Am. Chem. J.*, **46**, 544 (1911).

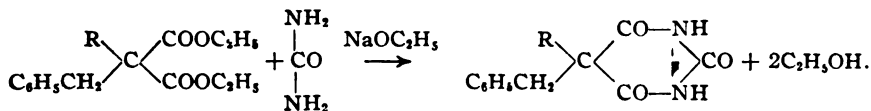
<sup>3</sup> Ger. pat. 293,163, 1916.

<sup>4</sup> Fischer and Dilthey, *Ann.*, **334**, 337 (1904).

<sup>5</sup> Hoerlein, U. S. pat. 1,025,526, 1912.

by Conrad and Bischoff<sup>6</sup> by methylating the benzyl derivative and by benzylating the methyl derivative, the product being identical in both cases. Although we employed both methods, we found it advantageous to put the benzyl group in first. The reason for this will be seen from the fact that in the preparation of a mono-substituted malonic ester a di-substituted derivative is invariably formed as a by-product except in the case of secondary alkyl radicals and a corresponding amount of ethyl malonate remains unsubstituted. With the lower alkyl radicals the boiling points of the three substances lie rather closely together, and consequently a purification of the ethyl mono-alkylmalonate requires repeated fractionation. On the other hand, the monobenzylmalonate is easily separated from the dibenzyl derivative and the unsubstituted ethyl malonate. When making the second substitution, however, an excess of alkyl halide may be used to advantage so as to bring the reaction to completion. By benzylating an impure lower mono-alkylmalonate with an excess of benzyl chloride the benzyl alkylmalonate is also easily separated from the other impurities but the yield from the malonic ester used is considerably less.

These di-substituted malonic esters readily condense with urea in the presence of sodium ethylate at 100–105°, yielding the sodium salt of the di-substituted barbituric acid, from which the free acid is obtained by acidifying with hydrochloric acid.



### Experimental Part

**Preparation of the Esters.**—Ethyl ethylbenzylmalonate was prepared by treating ethyl benzylmalonate with ethyl bromide and sodium ethylate in absolute alcohol. The other esters were prepared by treatment of the ethyl alkylmalonates with benzyl chloride in the same manner. We believe the first method is the more satisfactory. After completion of the reaction the alcohol was removed by distillation and the sodium chloride or bromide by shaking the residual oil with water. The product was dried with calcium chloride and purified by distillation *in vacuo*. Since the alkylbenzylmalonic esters were regarded merely as intermediates in the preparation of the corresponding barbituric acids, they were not analyzed or fractionated for the purpose of determining the exact boiling points. The product collected over a 10° range was considered pure enough for our purpose. Identification was made through the barbituric acids which were carefully purified by recrystallization.

<sup>6</sup> Conrad and Bischoff, *Ann.*, 204, 177 (1880).



Ester	Fraction collected	Pressure	Yield
	° C.	Mm.	%
Ethyl methylbenzylmalonate.....	165-175	15	63
Ethyl ethylbenzylmalonate.....	160-170	9	72
Ethyl <i>isopropyl</i> benzylmalonate.....	170-180	12	23
Ethyl <i>n</i> -butylbenzylmalonate.....	177-185	10	65
Ethyl <i>isobutyl</i> benzylmalonate.....	177-187	10	47
Ethyl <i>isoamyl</i> benzylmalonate.....	180-190	10	75

**Condensation of the Esters with Urea.**—A uniform procedure was followed except in the case of the *n*-propyl derivative where the benzyl group was introduced directly into *n*-propyl barbituric acid. A mixture consisting of 10 g. of the ester, three times the molecular equivalent of sodium dissolved in 20 parts of alcohol, and 1.5 moles of urea was heated in an autoclave at 105° for 5 hours. The resulting white mass consisting mainly of the sodium salt of the di-substituted barbituric acid was treated with a slight excess of hydrochloric acid and the alcoholic solution filtered from the sodium chloride. The filtrate was evaporated on the steam-bath until crystals began to form, and then cooled. Addition of water to the mother liquor gave a further yield. One or two recrystallizations from benzene containing a little alcohol gave a pure white product.

The *n*-propyl derivative was prepared by heating under a reflux condenser for 5 hours an alcoholic solution of *n*-propyl-barbituric acid with the calculated amounts of benzyl chloride and ammonium acetate. Ammonium chloride gradually separated from the alcoholic solution and the latter on evaporation gave *n*-propylbenzyl-barbituric acid, which was purified by recrystallization.

Of the following derivatives, *isopropylbenzyl-barbituric acid* has been previously described and a melting point of 230° reported.<sup>7</sup>

Substance	M. p.	Nitrogen			Yield
		Calc.	Found		
Barbituric acid derivative	° C.	%	%	%	%
5,5-methylbenzyl.....	207	12.07	12.01	11.94	74
5,5-ethylbenzyl.....	206-7	11.38	11.44	11.30	79
5,5- <i>n</i> -propylbenzyl.....	210	10.77	10.85	10.99	51
5,5- <i>isopropyl</i> benzyl.....	229	10.77	10.64	10.57	56
5,5- <i>n</i> -butylbenzyl.....	195	10.22	10.22	10.22	95
5,5- <i>isobutyl</i> benzyl.....	255	10.22	10.36	10.29	89
5,5- <i>isoamyl</i> benzyl.....	194-6	9.72	9.42	9.49	94

In this series the solubility in water decreases and the solubility in alcohol increases with increasing size of the alkyl group. All are soluble in dil. alkali. All have a bitter taste which is most pronounced in the lower members. The ethyl derivative showed the strongest hypnotic action

<sup>7</sup> Ger. pat. 293,163, 1916.

but this was accompanied by symptoms of tetanus. It is doubtful therefore whether any of these derivatives will be of therapeutic value.

### Summary

From the ethyl esters of alkylbenzylmalonic acids, urea and sodium ethylate, a series of alkylbenzyl-barbituric acids was prepared by the "veronal" synthesis.

In this series, ethylbenzyl-barbituric acid was found to have the strongest physiological action. Contrary to our expectations, the hypnotic effect was accompanied by symptoms of tetanus instead of the anti-spasmodic effect commonly attributed to the benzyl group.

DETROIT, MICHIGAN

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[CONTRIBUTION FROM THE KENT CHEMICAL LABORATORY OF THE UNIVERSITY OF CHICAGO]

## C<sub>18</sub> FATTY ACIDS. V. MOLECULAR REARRANGEMENTS IN SOME DERIVATIVES OF UNSATURATED HIGHER FATTY ACIDS

BY BEN H. NICOLET AND JOSEPH J. PELC<sup>1</sup>

Received January 28, 1922

The hydroxamic acids belonging to the aromatic and saturated aliphatic series are well known. Their properties and reactions have been carefully studied by Lossen,<sup>2</sup> Hofmann,<sup>3</sup> Hantzsch,<sup>4</sup> Werner,<sup>5</sup> and others. Their formation from esters and hydroxylamine is recognized as a quite general reaction.<sup>6</sup>

The rearrangement of unsaturated hydroxamic acid derivatives does not appear to have been investigated. A certain amount of work<sup>7</sup> has, however, been done on the rather analogous Hofmann rearrangement, and the general conclusion is that, at least for amides having the double bond in the  $\alpha,\beta$ -position, the reaction usually proceeds normally and without complications.

It is the purpose of the present paper to show that the rearrangements characteristic of hydroxamic acids and their derivatives take place, in general, normally, for the derivatives of oleic, elaidic and ricinoleic acids. Certain abnormal and rather surprising results were, however, also obtained.

<sup>1</sup> The material here presented is used by Joseph J. Pelc in partial fulfilment of the requirements for the degree of Doctor of Philosophy in the University of Chicago.

<sup>2</sup> Lossen, *Ann.*, **150**, 314 (1869); **161**, 347 (1872); **175**, 271 (1875); **186**, 1 (1877); **252**, 170 (1889); **265**, 176 (1891); **281**, 169 (1894); etc.

<sup>3</sup> Hofmann, *Ber.*, **15**, 412 (1882); **22**, 2854 (1889).

<sup>4</sup> Hantzsch, *ibid.*, **27**, 799, 1256 (1894).

<sup>5</sup> Werner, *ibid.*, **25**, 27 (1892); **26**, 1561 (1893); **29**, 1155 (1896).

<sup>6</sup> Jeanrenaud, *ibid.*, **22**, 1270 (1889).

<sup>7</sup> Jeffreys, *Am. Chem. J.*, **22**, 43 (1899). Weerman, *Rec. trav. chim.*, **26**, 203 (1907). Rinkes, *ibid.*, **39**, 200 (1920).

The Lossen rearrangement yielding the corresponding ureas was obtained in every case tried. Certain of the compounds thus formed may be of use in identifying substances which are otherwise oils or very low-melting solids. The Lengfeld-Stieglitz rearrangement, giving urethanes,<sup>8</sup> was also successful in all cases. In these reactions the double bond apparently had no effect whatever on the course of the reaction and was not affected by it, although the physical properties of some of the substances concerned made the reactions take place somewhat more slowly than usual.

It was therefore all the more unexpected that the preparation of isocyanates from oleo- and elaidohydroxamic acids by warming them with an excess of acetic anhydride led, whichever acid had served as starting point, to a mixture of *cis*- and *trans*-heptadecylenyl isocyanates. This was definitely proved by the isolation, in each case, of both the possible urethanes and monophenyl ureas. The actual separation of the two isocyanates did not prove feasible. It is of interest to note, in this connection, that acetic anhydride is not recorded as a reagent capable of converting oleic into elaidic acid, or *vice versa*. Furthermore, the urethanes when treated with acetic anhydride under the same conditions showed no tendency to rearrange to form geometrical isomers.

The possibility that this rearrangement at the double bond may have taken place under the influence of a shock to the molecule as a whole, involved in the rearrangement taking place to form the isocyanate radical is, however, rendered rather remote by the fact that a corresponding change does not take place during the Lossen and Lengfeld-Stieglitz rearrangements mentioned above, in each of which the accepted explanation involves the assumption of isocyanates as intermediate products. The present observation remains, therefore, an unexplained fact which will require consideration in any future discussion of the mechanism of rearrangements of the types under consideration here.

### Experimental Part

**Oleo-hydroxamic Acid.**—This acid has been described by Morelli<sup>9</sup> who prepared it from triolein. For its preparation, 15 g. of hydroxylamine hydrochloride in 100 cc. of hot alcohol was treated with a solution of 9.2 g. of sodium in 100 cc. of alcohol, and the mixture added to a solution of 62 g. of ethyl oleate in 200 cc. of alcohol. After heating under a reflux condenser for 2 hours most of the alcohol was removed by distillation and a considerable excess of 15% hydrochloric acid added. After filtration the product was recrystallized from alcohol (acetone is also good). Various modifications of the process gave no better results.

**Elaido-hydroxamic Acid.**—Prepared from ethyl elaidate by a method similar to that already described, this acid formed white flakes, m. p. 86°. It is less soluble in alcohol than is the oleo derivative.

<sup>8</sup> Lengfeld and Stieglitz, *Am. Chem. J.*, **15**, 215, 504 (1893); **18**, 751 (1896). Stieglitz, **29**, 49 (1903).

<sup>9</sup> Morelli, *Zentr.*, **1908**, II, 1019.

*Analysis.* Calc. for  $C_{18}H_{31}O_2N$ : N, 4.71. Found: 4.70.

**Ricinoleo-hydroxamic Acid.**—Ethyl ricinoleate was prepared from the fatty acids of castor oil without special purification. From this the hydroxamic acid was made in the usual way. It crystallizes from ether in white flakes, m. p. 65°.

*Analysis.* Calc. for  $C_{18}H_{31}O_3N$ : N, 4.47. Found: 4.41, 4.38, 4.41.

**Linolo-hydroxamic Acid.**—Ethyl linolate, prepared from linolic acid regenerated from the tetrabromide, was used for this preparation. The product obtained melted at 8–10°, and darkened and resinified on standing, doubtless due to oxidation. No additional derivatives were prepared.

*Analysis.* Calc. for  $C_{18}H_{31}O_2N$ : N, 4.74. Found: 4.69, 4.68, 4.71.

**Oleo-acetylhydroxamic Acid.**—In the acetylation, 10 parts of dry acetone was used as solvent, and only a very slight excess of anhydride. The solution should not be too concentrated. After heating under a reflux condenser for 0.5 hour, the solvent was evaporated. Recrystallized from alcohol, the product melted at 63°.

*Analysis.* Calc. for  $C_{20}H_{37}O_3N$ : N, 4.19. Found: 4.17, 4.15, 4.14.

**Elaido-acetylhydroxamic Acid.**—Prepared as above, this acid forms silvery flakes from alcohol, m. p. 84°.

*Analysis.* Calc. for  $C_{20}H_{37}O_3N$ : N, 4.19. Found: 4.12.

**$\lambda$ -Acetyl-ricinoleo-acetylhydroxamic Acid.**—Two mols of acetic anhydride are required in this case, as the hydroxyl of the ricinoleyl radical is also acetylated. The product, which was not completely purified, was an oil at ordinary temperatures. On cooling, it solidified, and melted at 6–8°.

*Analysis.* Calc. for  $C_{22}H_{39}O_4N$ : N, 3.52. Found: 3.48, 3.46, 3.50.

**Oleo-diacetylhydroxamic Acid.**—Attempts to introduce both acetyl groups in a single operation, usually resulted in mixtures containing various amounts of isocyanates (see later). Better results were obtained by dissolving the mono-acetyl derivative in acetone, and warming gently with one mol of anhydride. The product forms shining plates from alcohol, m. p. 64–5°. As expected, it does not rearrange in alkaline solution.

*Analysis.* Calc. for  $C_{22}H_{39}O_4N$ : N, 3.67. Found: 3.64, 3.62, 3.64.

**Elaido-diacetylhydroxamic Acid.**—This acid, m. p. 82°, is very similar in preparation and properties to the one just described.

*Analysis.* Calc. for  $C_{22}H_{39}O_4N$ : N, 3.67. Found: 3.62, 3.60, 3.62.

**Lossen Rearrangement; Formation of Ureas.**—This rearrangement takes place perfectly normally on warming the mono-acetyl hydroxamic acids described above with aqueous alkali, according to the equation  $2RCONHOCOCH_3 + K_2CO_3 = RNHCONHR + 2KOCOCH_3 + 2CO_2$ . However, on account of the very slight solubility of the acids themselves, a considerable excess of normal carbonate solution (35–70 cc. per g. of acid) is necessary for complete solution. After warming for 0.5 hour on a water-bath the solution becomes cloudy, and the addition of a few drops of hydrochloric acid (sometimes not necessary) causes the urea to separate.

**Di-trans-heptadecylenyl Urea.**<sup>10</sup>—The product obtained as described above from oleo-acetylhydroxamic acid, was a solid from which impurities could be removed by extracting with warm alcohol, in which the urea itself was very insoluble. The product, crystallized from chloroform, formed needles, m. p. 59°.

<sup>10</sup> Michael, *J. prakt. Chem.*, [2] 52, 349 (1895), is inclined to classify oleic and elaidic acids as maleinoid and fumaroid forms respectively; see also, *ibid.*, 38, 1 (1888) and 46, 209 (1892). Without any intention of entering this controversy, the term "*trans*" is used in this paper to refer to derivatives of the oleic acid type, and "*cis*" for derivative directly related to elaidic acid, merely as a matter of reference.

*Analyses.* Calc. for  $C_{33}H_{55}ON_2$ : N, 5.36. Found: 5.29, 5.25, 5.26.

**Di-*cis*-heptadecylenyl Urea.**—This substance was prepared from elaido-acetylhydroxamic acid in the same way as described for the *trans* compound. It melted at 92–93°.

*Analyses.* Calc. for  $C_{33}H_{55}ON_2$ : N, 5.36. Found: 5.28, 5.24, 5.26.

**Dihydroxy-heptadecylenyl Urea.**—Acetyl-ricinoleo-acetylhydroxamic acid treated as described above, yields an oily liquid. Analysis shows that the  $\lambda$ -acetyl group is not completely removed in this reaction. On warming the product with 10% caustic alkali at 80–90° the hydrolysis of the remaining acetyl group is completed, and the product, recrystallized twice from alcohol, melted at 57.5°.

*Analysis.* Calc. for  $C_{33}H_{55}O_3N_2$ : N, 4.96. Found: 4.92.

**Preparation of Urethanes.**—The proper acetylhydroxamic acid, carefully dried, is treated with one equivalent of sodium dissolved in absolute alcohol, and warmed for 20 minutes at a suitable temperature. The alcohol is then removed, for the most part, by distillation, and the urethane dissolved in hot 70° ligroin, filtered from sodium acetate, and crystallized.

***Trans*-heptadecylenyl Urethane.**—Oleo-acetylhydroxamic acid was warmed with sodium ethylate at 40° as described; the product from ligroin melted at 42–43°.

*Analyses.* Calc. for  $C_{30}H_{51}O_2N$ : N, 4.30. Found: 4.23, 4.17, 4.20, 4.18, 4.22.

The corresponding methyl ester, methyl *trans*-heptadecylenyl carbamate, melted at 40–41°.

***Cis*-heptadecylenyl Urethane.**—The elaido-acetylhydroxamic acid was heated at 70° as described, and the alcohol distilled. When the ligroin is cooled in a freezing mixture, the yield is almost quantitative. The urethane melted at 87–88°.

*Analysis.* Calc. for  $C_{30}H_{51}O_2N$ : N, 4.30. Found: 4.25.

The corresponding methyl ester, methyl *cis*-heptadecylenyl carbamate, melted at 85–86°.

In none of these reactions was there any sign of inversion at the double bond.

**Heptadecylenyl Isocyanates from Oleo-hydroxamic Acid.**—A saturated solution of the hydroxamic acid in acetone was prepared and rather more than two mols of acetic anhydride added. The solution was warmed on the water-bath for 10–15 minutes, the acetone evaporated, and the residue dissolved in ligroin. After crystallizing from this solvent a good yield was obtained of a white crystalline product, rather stable even in air. The following table shows the effect of variations in time of heating 6 g. of sample, and in quantity of anhydride.

No.	Time Min.	Anhydride G.	Melting point °C.	No.	Time Min.	Anhydride G.	Melting point °C.
1	5	1	48–60	4	10	1	59–68
2	5	1.5	60–70	5	15	1	66–84
3	5	2	65–80				

The first figure under "melting point" is in each case the point at which melting begins, and the last point that at which fusion is complete. As, however, variable amounts of the *trans*-acetyl derivative are always present, these figures have little significance. No *cis*-acetyl derivative was ever found. Mixture 5, after several recrystallizations, melted at 48–52°. This product gave no test with ferric chloride for hydroxamic acids.

*Analysis.* Calc. for  $C_{18}H_{33}ON$ : N, 5.02. Found: 4.93.

Its behavior with alcohol and with aniline leaves no doubt that this product is

essentially a mixture of *cis*- and *trans*-heptadecylenyl isocyanates. It was not found possible to separate these two isocyanates. When, however, a portion of the mixture was gently warmed with absolute alcohol, solution and reaction took place, and it was possible to isolate by fractional crystallization, both *cis*- and *trans*-heptadecylenyl urethanes, melting at 87–88° and 41–42°, respectively. The identities of these substances were confirmed by analyses, and by the fact that the melting points were not lowered when the urethanes obtained by this method were mixed with those obtained by the Lengfeld-Stieglitz rearrangement.

By way of further confirmation, the isocyanate mixture was slightly warmed with an excess of aniline. The product, after a rather tedious process of fractional crystallization from alcohol, yielded two substances, m. p. 72–73° and 83–84°, both of which, after heating at 150° with hydrochloric acid, gave tests for aniline. There is no doubt that these are the two heptadecylenyl ureas; and it is considered highly probable that the higher-melting product is, as usual in this series, the *cis* compound.

*Analyses.* Calc. for  $C_{24}H_{48}ON_2$ : N, 7.58. Found, for *cis*-urea: 7.54, 7.47, 7.50, 7.49. Found, for *trans*-urea: 7.51, 7.54, 7.50.

**Heptadecylenyl Isocyanates from Elaido-hydroxamic Acid.**—The reaction was very similar to that described above. The yield was less good, and heating for about 45 minutes seemed to be necessary. A product was again isolated which had the composition of a mixture of isocyanates (N, calc. 5.02%; found, 4.94, 4.90%) but which melted rather higher than the similar product previously described (72–82°).

On treatment with alcohol this product gave two urethanes which were identical with those already described. The proportion of *cis*-urethane was, however, distinctly greater in this case.

Similarly, with aniline, a product yielding *cis*- and *trans*-heptadecylenyl phenylureas, identical with those described above, was obtained. Because the isocyanate mixture from elaido-hydroxamic acid had a markedly higher melting point, and also gave a much smaller yield of the *trans*-urethane, it is considered that this mixture contained a larger proportion of the *cis*-isocyanate than did the other. This would also imply that an equilibrium was not reached between the two isocyanates. Such a result would not be surprising, however, as under the conditions of the reaction, a number of competing processes are taking place (*e. g.*, the formation of diacetyl derivatives).

### Summary

1. Unsaturated fatty acids (oleic, elaidic, linolic, ricinoleic) form hydroxamic acids as do aromatic and saturated aliphatic acids.

2. The Lossen rearrangement, giving ureas, is not affected by, and does not affect, the double bond.

3. The same applies to the Lengfeld-Stieglitz rearrangement, giving urethanes.

4. The supposedly analogous rearrangement to isocyanate, using acetic anhydride, is complicated by the fact that a mixture of *cis*- and *trans*-isocyanates results, whichever pure hydroxamic acid (oleo- or elaido-) is used.

CHICAGO, ILLINOIS

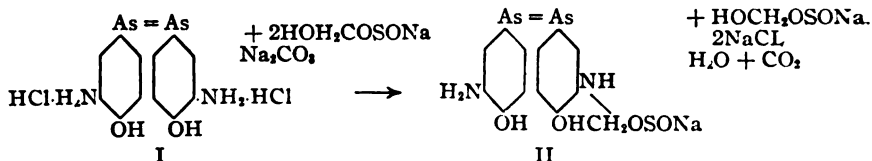
[CONTRIBUTION FROM THE LABORATORIES OF THE UPJOHN COMPANY]

## TOXICITY OF NEO-ARSPHENAMINE

BY MERRILL C. HART AND WILBUR B. PAYNE

Received March 6, 1922

The basic patent<sup>1</sup> of Korndorfer and Reuter describes the production of a neutral solution of a derivative (II) of arspenamine (I) derived by condensation with sodium formaldehyde sulfoxylate.



The first motive for this preparation was the hope that this solution would be more easily prepared than that of the phenolate made by treating (I) with an excess of sodium hydroxide. As a matter of fact, the solution is much more difficult to produce and is unstable, but is found in practice to be much less toxic.

In order to make this much less toxic derivative available clinically it was necessary to produce a dry powder, and this proved a matter of considerable difficulty. So readily is it oxidized that it is not advisable to increase the manipulations for the purpose of purification of the intensely soluble derivative. The commercial product is a pharmaceutical mixture of the reaction products containing 18–20% arsenic rather than a chemical individual of 32% arsenic.

The pharmacological examinations (with rats) at the Hygienic Laboratory<sup>2</sup> showed that while imported neo-arsphenamine was at first being tested at 90 mg./kg., the standard minimum tolerated dose which rats should survive should be increased to 180 mg./kg. This was later increased to 200 mg./kg. It may be doubted if the neo-arsphenamine first imported into this country was examined in this respect, for with the first year of work the toxicity of this drug was greatly decreased.

Schamberg, Kolmer and Raiziss<sup>3</sup> showed that for commercial neo-arsphenamine the maximum tolerated dose varied from 180 to 300 mg./kg. or more (rat), the average tolerance being 254 mg./kg. Of 24 samples examined 5 were tolerated in doses above 300 mg./kg. In the recorded table only two rats are used for this test. Later these experimenters<sup>4</sup> reported the average of a large number of lots of neo-arsphenamine to be

<sup>1</sup> Korndorfer and Reuter, U. S. pat. 1,053,300 (1913). Reissue No. 13,848 (1914).

<sup>2</sup> *Hygienic Lab. Bull.*, 113, (1918): 3 samples passed tests at 100, 175 and 150 mg./kg.

<sup>3</sup> Schamberg, Kolmer and Raiziss, *Am. J. Med. Sci.*, 160, 197 (1920).

<sup>4</sup> Schamberg, Raiziss and Kolmer, *J. Am. Med. Assoc.*, 78, 6, 402 (1922).

280 mg./kg. Roth<sup>6</sup> reports a sample which was tolerated in doses of 420 mg./kg. and had an arsenic content of 19.5%. Another sample (18.8% arsenic) from the same source was tolerated in doses of 280 mg./kg. There is, therefore, a great variability in the toxicity of various products when studied by this method. We may add that we do not believe that these figures convey any clinical significance unless they fall below 200 mg./kg.

What is the cause of this variability? In the first place, the difference in arsenic content has an influence. A sample containing 20% of arsenic and borne at 280 mg./kg. would be tolerated at 310 mg./kg. had it contained only 18%. Second, there is a variability in the tolerance of the albino rats used. This may amount to 100 mg./kg., as we will show in the experimental part. Third, Raiziss and Falkov<sup>6</sup> have indicated that the analyses of various samples show the presence of considerable quantities of the dimethylene sulfinic acid derivative. In the "neo" derivative having Formula II the ratio of arsenic to sulfur should be 2:1, while if two groups were substituted it would of course be 2:2. A finding of 2:1.4 as found in several samples would indicate a mixture of 60% of the mono-, with 40% of the disubstituted arsenical. In view of the well-known decrease in toxicity produced by replacing an amino hydrogen by an acidic radical (*e. g.*, acetanilide from aniline) it would appear that this consideration may be of importance in the variability. Macallum<sup>7</sup> on the contrary reports that "analysis of best preparations has indicated that it is not possible to form products of sulfoxylate:arsenic ratio exactly 1:2, but that products closely approximating to this are quite practicable." Furthermore, neither of these papers contains toxicity determinations of the material analyzed.

What appeared at first to be another important factor in producing variability in neo-arsphenamine was the toxicity of the original arsenical. Arsphenamine itself is not used for the commercial production of neo-arsphenamine. This is prepared from the base which is dissolved in the requisite amount of hydrochloric acid. The base is readily oxidized upon exposure, and the variable nature will be disclosed by the toxicological examination of the hydrochloride. This preparation is, however, produced in rather remarkably uniform quality. Schamberg, Kolmer and Raiziss<sup>8</sup> examined 22 samples which were tolerated in doses varying from 90 mg./kg. to above 120 mg./kg. The average tolerated dose was 0.105 g. per kg. The government requirement of 100 mg./kg. is a high requirement, and in fact is probably not always passed in production. In our opinion the 90 mg./kg. requirement is a more reasonable one. Christiansen<sup>8</sup>

<sup>6</sup> Roth, *U. S. Pub. Health Repts.*, 35, No. 38, 2208 (1920). *Arch. Derm. Syph.*, 2, 300 (1920).

<sup>8</sup> Raiziss and Falkov, *J. Biol. Chem.*, 46, 209 (1921).

<sup>7</sup> Macallum, *THIS JOURNAL*, 43, 643 (1921).

<sup>8</sup> Christiansen, *ibid.*, 43, 2204 (1921).



reports a finding of 110 mg./kg. as the average. This drug as marketed is quite stable and uniform and white rats react to it acutely in a most definite manner. We have shown that using arsphenamine varying in toxicity from 90 mg./kg. to 130 mg./kg. there is no corresponding variation in the toxicity of the resulting neo-arsphenamine.

According to King<sup>9</sup> the variable sulfur found in arsphenamine is partly sulfate and partly 3,3'-diamino-4,4'-dihydroxy-5-sulfo-arsenobenzene hydrochloride. It is reported as being more toxic than arsphenamine (mice). This "nuclear" sulfur would of course introduce a second factor into the ratio of arsenic to sulfur in the "neo" derivative. This factor can be demonstrated by distinguishing between sulfoxylic sulfur, and nuclear sulfur (the sum being total sulfur). While sulfonation always results to a slight extent in the production of arsphenamine, this side action is more pronounced in the production of neo-arsphenamine.

In our experimental work, two sets of experiments were conducted: small scale experiments, in which the mechanical factors such as filtration and desiccation were eliminated; and semi-commercial (50-100 tubes) experiments in which we could compare the errors involved in various mechanical procedure.

In this paper the former control experiments are reported, and it will be observed that when the rats used for testing are normal and when mechanical errors are avoided neo-arsphenamine is quite a constant product and is tolerated in doses of 320 to 355 mg./kg. for 20-18% material. In another paper we will take up briefly the second series of experiments, and the chief source of variability.

### Experimental

**Market Conditions.**—Our laboratory results agree with those mentioned above. We made a special endeavor to find a sample comparable to the high test sample reported by Roth. We followed the official method and excluded unfit rats by means of weight curve. We find that 360 mg./kg. is a maximum figure. This product was, therefore, one in which commercial production is perfected under ideal conditions. We report a typical series of results.

TABLE I  
TOLERATED DOSES IN MG./KG. OF COMMERCIAL SAMPLES

Sam- ple	% As	200	240	280	320	360	400	M. T. D. mg./kg.
A	19.0				++++			280
B	18.7		+++	+++	+++	++++-	----	360
C	18.9	+++	+++		---			280
D	20.2			+++	+++++	++++-	----	360
E	19.0		++---	----	++			290
F	18.5				+++++			320
G	18.5				6L; 2D			320
+ Lived. - Died.								

<sup>9</sup> King, *J. Chem. Soc.*, 119, 1107, 1416 (1921).

The variability as indicated ranges from 200 to 360 mg./kg. The test on "E" is inaccurate due to change in test animals. This is a serious matter, because the determination of such a value as the maximum tolerated dose is sufficiently defective even when the same stock is used.

**Standardization of White Albino Rats.**—In any pharmacological work it is important to ascertain results by comparison. Thus in assaying digitalis, crystalline ouabain forms a basis for comparison. In pituitary work histamine is used. In this work the test animals offer an element of variability which hitherto has not been rigidly controlled.<sup>10</sup>

The dimensions of the error which may result by making the same test on different rats are indicated below.

TABLE II  
VARIATION IN RESISTANCE TO SAME DOSES IN MG./KG.

Sample	200	240	280	300	320	360	Discrepancy
M 138	13 <sup>+</sup> ; 0 <sup>-</sup>	12 <sup>+</sup> ; 0 <sup>-</sup>	10 <sup>+</sup> ; 1 <sup>-</sup>	+++++			Over 100 mg./kg.
Ditto <sup>a</sup>	10 <sup>-</sup> ; 0 <sup>+</sup>						
M 168	+++++	+++++	++---				About 40 mg./kg.
Ditto	+++--						
H 187 <sup>b</sup>			++---		-----		About 40 mg./kg.
Ditto			+++++		++++-	5 <sup>+</sup> , 5 <sup>-</sup>	

<sup>a</sup> Run independently by another pharmacologist. With different rats the tests at 200 mg./kg. were satisfactory.

<sup>b</sup> Control rats of this batch sacrificed and autopsied showed heavy infection with *B. bronchosepticus* which lowered their resistance.

On the other hand, it is true that while the test animals vary they are quite uniform in most cases. Roth<sup>11</sup> suggests the possibility of seasonal variation in the resistance of rats, stating that they are perhaps more resistant to neo-arsphenamine during the summer than during the winter. It does not appear that an accurate estimate of the factor of deterioration can be made unless the test animals are standardized, *i. e.*, unless the tests at different dates are made comparatively against a standard.

At the present time it is impossible to accept a sample of neo-arsphenamine as a control. Not to speak of deteriorative possibilities, there are unavoidable variations in arsenical content. The work of Raiziss proves the possibility of other chemical variations. Furthermore, the real object of the official test is to limit the oxidation of the product through mechanical errors in manufacture. Hence it appeared to us that a suitable standard would be a 4% solution of neo-arsphenamine (20% arsenic) prepared from analyzed arsphenamine in such a way that all manipulative errors are eliminated. By using the conditions of the experiment on p. 1154 a solution results which when injected is tolerated in doses of 320 mg./kg. This we consider a standard. In our work we have discarded all rats in

<sup>10</sup> See Hooper, Kolls and Wright, *J. Pharmacol.*, **18**, 141 (1921).

<sup>11</sup> Roth, *U. S. Pub. Health Repts.*, **36**, No. 41, 2538 (1921).

which more than one death in 5 tests resulted at 280 mg./kg. (see, *e. g.*, H-187, Table II).

**Maximum Tolerated Dose of Neo-arsphenamine.**—This was determined by use of the apparatus in Fig. 1. The object was to prepare in the calibrated 100cc. flask A, a 4% solution of neo-arsphenamine (20% of arsenic).

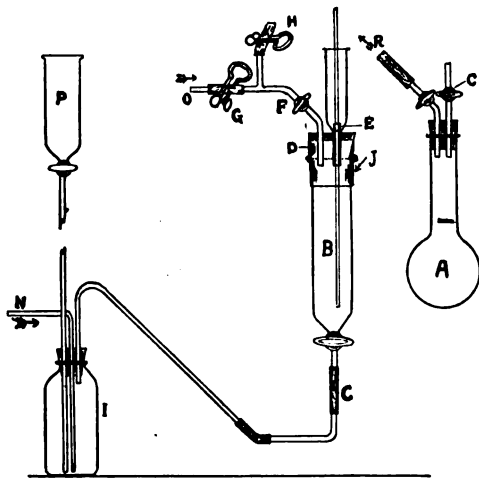


Fig. 1.—Apparatus for preparation of standard solutions.

other opening in the stopper bears a stopcock F, which connects through G with a gasometer of nitrogen, and with an outlet at H. All the nitrogen is carefully washed with an alkaline hydrosulfite solution. As there is occasionally a trace of air in compressed nitrogen, and since the same is more frequently true for carbonic acid, this requires attention.

The apparatus and tubes are swept out with nitrogen gas. Then F is left open and H is opened but G is closed. The weighed arsphenamine (2.581 g. for 31% material) is dusted into the pipet, the glass rod removed for the time being and the material dissolved in the agitated methyl alcohol. The pipet is brushed out and rinsed with a few drops of methyl alcohol and dried and the rod fitted loosely into place. By slipping along the rubber tubing the rod can be used to break up any gummy masses of the hydrochloride which may form.

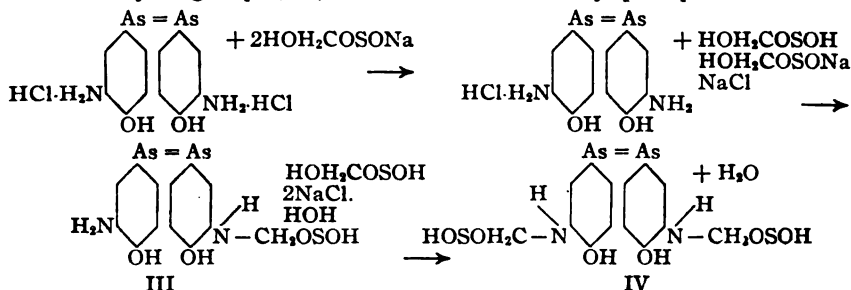
Long standing at this point causes the separation from the alcohol of the sulfur-containing impurities, so when solution is completed, H is closed and G opened and the cylinder is placed in a thermostat at 25°. The calculated quantity (1.95 cc. of 100% solution) of analytically pure<sup>12</sup> sulfoxylate is added, allowed to drop in by releasing H, and a few drops of water are used to rinse the tube. E is fitted tightly into position and the reaction proceeds. The calculated quantity of 10% sodium carbonate solution is finally added at E and allowed to run in by opening H.

The nitrogen is turned off at C and the reaction cylinder after removal from the thermostat is connected with the nitrogen-filled bulb A which is wired on. A is evacuated (through R) to 10–15 mm. and, after closing E and H and opening G, the solution

<sup>12</sup> Heyl and Greer, *Am. J. Pharm.*, 94, 80 (1922).

of the neo-arsphenamine is drawn into A, nitrogen gas from the gasometer through O displacing it. Most of the methyl alcohol is lost by evaporation, while the cylinder is quantitatively rinsed with air-free water added at E with the exclusion of all air. This is readily and perfectly accomplished by keeping G and F open and opening H only when it is desired to allow liquid to flow at E. It is convenient to use the rod as a policeman. Finally, the brilliantly clear solution is made up exactly to the mark, a layer of toluene run over it and it is ready for the toxicological tests.

With this apparatus we now varied a number of conditions and observed the effect on toxicity. It is stated in the patent literature<sup>13</sup> that if one uses an alcoholic medium instead of an aqueous one there is a decreased toxicity. Another variation consists in operating with the precipitating base rather than the hydrochloride. When working in alcoholic solution the reaction involved two dissolved substances, *i. e.*, hydrochloride and the sulfoxylate. The latter functions in two ways. First, it liberated the amino group, which promptly reacts with the sulfoxylic acid and the free "neo" acid with one sulfoxylic group (III) is almost immediately precipitated.



As this acid (III) is insoluble in alcohol and in water, this factor controls the reaction and a fairly uniform product is formed. The product is quantitatively precipitated in less than 5 minutes and greatly increasing the time does not conspicuously alter the pharmacological or chemical findings.

In view of the discovery of Raiziss and Falkov<sup>6</sup> of a considerable admixture of the dimethylenesulfinate derivative in some samples, we endeavored to form this material by raising temperature, or increasing time, or increasing volume of medium, the idea being to render the precipitate at first formed somewhat more soluble and thus assist in the introduction of the second group, giving the disubstituted derivative (IV).

These changes immediately complicate the product with by-products. These do not appear to consist entirely of the dimethylene-sulfinate derivative. Instead, the sulfur enters the ring.

Since the aqueous alkaline medium favors the solution of the reaction product, several experiments were run in which the sulfoxylate had ample opportunity to react beyond the first stage but this did not favorably affect the product.

<sup>13</sup> Ger. pat. 260,235, 1913. Compare Ger. pat. 245,756, 1912.

The following table of reactions in methyl alcohol indicates the fact that the reaction is practically completed in 10 minutes. When the temperature is raised even to 35° for 30 minutes discoloration and increased toxicity result.

TABLE III  
METHYL ALCOHOLIC SOLUTION-ACID SOLUTION  
Condition of reaction

Expt.	Arsphen-amine	Temp.		Vol. Cc.	Time Min.	As %	Doses: mg./kg.			
		° C.	Cc.				280	320	360	400
H-166	A-1	25	15	10	10	19.8	+++++	++++		
H-179	171	25	15	10	10	19.6	+++++	++++	++++	----
H-185	M	25	15	10	10	20.1	+++++	++++	5L:5D	
H-191	M	25	45	10	10	20.1	+++++	++++	++++	
H-196	M	35	15	10	10	19.8	+++++	++++	++++	
H-197	M	35	30	30	30	17.0		-----	-----	
H-182	171	50	15	10	10	19.7			++++	----
H-198	M	25	20	20	19.7	+++++	+++++	++++		

Found: Maximum Toxicity = 320 mg./kg.

The reaction was carried out once (Expt. 195) by dissolving the hydrochloride in 15 cc. of alcohol, precipitating the base with the calculated quantity of sodium carbonate solution (10%), adding the sulfoxylate and allowing the reaction to proceed, testing it at 30-minute intervals for complete solubility in dil. carbonate solution. After 3 hours the reaction had not gone to completion. The toxicity of this preparation was not determined.

In aqueous solution the following experiments were run.

TABLE IV  
AQUEOUS SOLUTION

Expt.	Arsphen-amine	Temp.		Vol. Cc.	Time Min.	As %	Doses: mg./kg.			
		° C.	Cc.				280	320	360	400
H-193	M	25	45	10-30 <sup>a</sup>	20	20.3	++++	++++	-----	
H-138	138	25	15(50% alc.)	20	20	18.7	++++	++++		
H-199	M	25	25	60	60	19.2	++++	-----	-----	++++

<sup>a</sup> After running the reaction for 10 minutes the calculated quantity of 10% sodium carbonate solution was added, after which a clear solution resulted in 25 minutes. The reaction was discontinued after 30 minutes.

The chief object of the experiments in aqueous solution was to learn whether the dimethylene-sulfinic acid derivative was produced in greater amount and how this affected the toxicity of the preparation. This might be expected to be less toxic. All the runs in both alcoholic and aqueous medium were subjected to the following analytical control.

**Analyses of the Products Tested Above.**—For this purpose 3 samples

of the solution of 5, 5 and 25 cc., respectively, were removed. Duplicate estimations of the arsenic were made by the Lehman method. For a 20% neo-arsphenamine 0.04 g. of arsenic (10.67 cc. of 0.1 *N* sodium thiosulfate solution) is required.

The 25cc. sample diluted to 70 cc. was cooled to 0° and precipitated with a slight excess of 2 *N* hydrochloric acid and then centrifuged. The precipitated neo-acid was washed thrice with 70 cc. of water at 0° acidulated with 2 cc. of 2 *N* hydrochloric acid, then centrifuged to obtain a sharp separation. The resulting free acid was dissolved in a slight excess of 2 *N* sodium hydroxide solution and made up to 50 cc. This was divided into 3 parts of 10, 20 and 20 cc., respectively. Ten cc. was used for the arsenic determination in the precipitated neo-acid. One of the 20cc. aliquot portions was used for the determination of total sulfur by the regular sodium peroxide fusion method. The other portion was used for the determination of all the sulfur except nuclear (sulfoxylate sulfur) by the method given by Raiziss and Falkov.<sup>6</sup> This involves oxidation with an excess of iodine solution and precipitation of barium sulfate.

The difference between total sulfur and sulfur by the iodine oxidation method may be taken as sulfur which has been introduced into the ring as a sulfonic acid derivative or united with the arsenic as an organic arsenic sulfide. The calculations are reported in terms of atomic ratios. Theory for the pure monomethylene-sulfinic acid derivative requires 2 arsenic : 1 sulfur. The findings are as follows.

TABLE V  
DISTRIBUTION OF SULFUR

Sample	Sulfur in original arsphenamine			Condensation			Sulfur distribution in neo-arsphenamine		
	Total S	S by iodine	Nuclear S	Solvent	Time Cc. Min.	Temp. ° C.	Total S	Neo. <sup>b</sup> S	Nuclear S
H-166	0.15	0.04	0.11	CH <sub>3</sub> OH.	15 10	25	1.15	1.06	0.09
H-179	0.15	0.07	0.08	CH <sub>3</sub> OH.	15 10	25	1.18	1.04	0.14
H-185	0.10	0.08	0.02	CH <sub>3</sub> OH.	15 10	25	1.27	1.18	0.09
							1.26	1.12	0.14
H-191	0.10	0.08	0.02	CH <sub>3</sub> OH.	45 10	25	1.21	1.15	0.06
H-196	0.10	0.08	0.02	CH <sub>3</sub> OH.	15 10	35	1.34	1.19	0.15
H-197	0.10	0.08	0.02	CH <sub>3</sub> OH.	30 30	35	1.37	1.23	0.14
H-182	0.15	0.07	0.08	CH <sub>3</sub> OH.	15 10	50	1.39	1.17	0.22
H-198	0.10	0.08	0.02	CH <sub>3</sub> OH.	20 20	25	1.39	1.25	0.14
H-193	0.10	0.08	0.02	HOH	15 10-30 <sup>a</sup>	25	1.18	1.04	0.14
H-199	0.10	0.08	0.02	HOH	25 60	25	1.30	1.16	0.14

<sup>a</sup> See Table IV.

<sup>b</sup> Neo-sulfoxylic sulfur.

These results show that when this reaction is carried out at 25° for ten minutes a relatively pure mono derivative is formed (4 to 15% of the di derivative being formed). When the time is doubled 25% of the

di compound is formed. Varying the dilution seemed to have no appreciable effect on the introduction of the methylenesulfinic acid group. Increasing the temperature  $10^{\circ}$  resulted in an increase in the di derivative (about 4%). A further increase up to  $50^{\circ}$  gave no greater percentage of the di compound. Increasing the time from 10 to 30 minutes at  $35^{\circ}$  gave a slight increase in the substitution (about 4%). When this reaction was carried out at higher temperature and longer times a secondary decomposition took place with more of the sulfur entering the nucleus, a marked coloration of the solution and a somewhat higher toxicity.

#### Influence of Toxicity of Intermediate Base on Toxicity of Resultant Neo-arsphenamine

We recognize the stability of arsphenamine, particularly in acid solution, but the base itself is more prone to oxidation. It would appear probable that this factor might have a final influence, particularly as neo-arsphenamine is prepared from base rather than hydrochloride. Since this work was originally outlined to study the last part of the preparation, (*i. e.*, the condensation of sodium formaldehyde sulfoxylate), only standardized hydrochlorides were used instead of the unstandardized base. It will be admitted that any irregularities in base production will be accentuated in the corresponding hydrochlorides, because it involves one further manipulation (*i. e.*, precipitation and desiccation of the product). In using hydrochlorides of various toxicities we have been astonished to find that a variability of 40 mg./kg. in the starting material has been without conspicuous influence upon the neo-arsphenamine solutions prepared therefrom.

The following determinations will show the nature of the starting material used in the above described experiments.

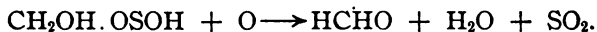
TABLE VI  
TOXICITY OF ARSPHENAMINE USED  
Doses: mg./kg.

Sample	As %	90	100	110	120	130
A-1	31.3	+++++	3L; 7D	++++		
171	30.8			+++++	+++++	++++
M	32.1		++++	++++	-----	

By comparing this table with Table III, it will be observed that a 19.6% of drug (H-179) made from the hydrochloride passing the tests at 130 mg./kg. makes a distinct failure at 400 mg./kg.; whereas the sample H-185 made from M which while just passing 100 mg./kg., gives an equally good neo derivative. Even A-1, failing to pass at 100 mg./kg. gives a neo derivative of standard tolerance.

One reason for this uniformity is probably found in the fact that the free sulfoxylic acid present in the reaction mixture in large amounts

must tend to eradicate traces of oxidation products, for the free acid is quite unstable, breaking down easily.



**The Lethal Activity of Neo-arsphenamine.**—The characteristic delayed effects which result in the official tests, make it advisable to extend the period during which the rats are under observation to 7 days. This is in marked contrast to the acute poisoning due to arsphenamine, for which the period of observation is but 2 days. Roth<sup>14</sup> has plotted a curve showing this difference between the drugs. With commercial arsphenamine the maximum number of deaths occurs on the first day, whereas the fourth day is the critical day for neo-arsphenamine poisoning.

In testing solutions of freshly prepared high test neo-arsphenamine, we find that toxic doses behave very similarly to arsphenamine itself. The acute lethal effect is at a maximum in 24 hours as is shown by the solid line curve in Fig. 2.

The findings of Roth<sup>14</sup> for the death rate of rats treated with commercial neo-arsphenamine (dry powder) is given by the broken line.

It would appear that when the mono derivative is prepared in pure condition and when traces of oxidation products are excluded, the toxic action of higher doses is acute. It should be noted in passing, where high test products such as B and D (p. 1152) are being tested a similar acute death rate frequently results.

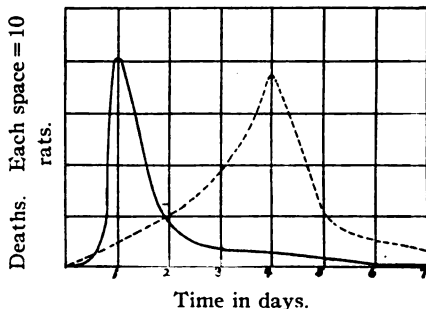


Fig. 2.—Difference in the death rate of rats after poisoning with solutions of freshly prepared, high test neo-arsphenamine and with the solid commercial product.

### Summary

1. The toxicity of commercial samples of neo-arsphenamine ranges from 200 to 360 mg./kg.

2. In determining the toxicity of neo-arsphenamine the variability of the test rats is a very important factor. Examples were given where 40 to 100 mg./kg. difference was obtained by the same test made on different animals.

3. A method is suggested which can be used for the standardization of the neo-arsphenamine test rats.

4. The toxicity of the arsphenamine (90–130) is shown to have a negligible effect on the toxicity of the neo-arsphenamine derived from it. In the condensation of arsphenamine to neo-arsphenamine the influence

<sup>14</sup> Roth, *Arch. Derm. Syph.*, 2, 295 (1920). See also Ref. 10.



is shown of the change of solvents, dilution, time, and temperature on the toxicity, introduction of the methylene-sulfinate group and sulfur distribution.

5. A curve is given showing the acute lethal activity of a freshly prepared solution of neo-arsphenamine.

6. The introduction of a methylene-sulfinic acid group in the arsphenamine increases the tolerated dose of the arsenical from 110 mg./kg. to about 320 mg./kg. (20% of arsenic). Introduction of the second group was complicated with side reactions giving a higher toxicity.

In conclusion we wish to thank Dr. Frederick W. Heyl at whose suggestion this work was carried out.

KALAMAZOO, MICHIGAN

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## NEW BOOKS

**Within the Atom.** A Popular View of Electrons and Quanta. By JOHN MILLS. D. van Nostrand Company, N. Y., 1921. xiii + 215 pp. 36 figs. 13 X 19.5 cms. Price, \$2.00 net.

The rapid advance that has been made in the past decade or two in the investigation of the structure of the atom, and which is still in full progress, has attracted the interest not only of scientists but also of the general reading public. Mr. Mills in undertaking the extremely difficult task of presenting the experimental results and theoretical conclusions of the subject in a form that will be popularly comprehended, has gone to unusual lengths in excluding everything of mathematical nature and in introducing elaborate illustrations drawn from everyday life. The result is a very readable book which appears to serve its purpose acceptably. While no attempt is made to furnish references to the literature, the reader is familiarized with the names of the principal investigators in the various fields considered.

The author has rather wisely disregarded historical order and with the assumption of some knowledge of a few of the fundamentals of physics and chemistry begins with the presentation of the electronic structure of the atom, and passes successively to isotopes, radioactive phenomena, conduction of electricity through gases, and general electronics. Atomic numbers are introduced through a consideration of X-radiation, the quantum theory through photo-electric effects; the structure of crystals as revealed by X-rays is simply and clearly presented. The final chapter is devoted to the consideration of energy and its availability. In an appendix several pages are given to an elementary exposition of the use of the decimal exponential system of writing numbers, which though undoubtedly necessary, is a rather sad commentary on our common school methods of teaching mathematics. The appendix contains definitions, magnitudes, and discussions of various units and terms employed

in the text. An alphabetical glossary takes the place of an index and contains abbreviated definitions of the technical terms employed. A few errors have crept in. One of the most serious is the confusing, on p. 9, of the terms "half life" and "average life" in radioactive changes.

S. C. LIND

**Elektrochemische Metallkunde** (The Electrochemistry of the Metals). By DR. R. KREMANN, Professor of Physical Chemistry at the University of Gratz. Second volume, 1st part, 3rd section of *Metallographie*. Gebrueder Borntraeger, Berlin, 1921. xx + 656 pages; 226 figures. 18.5 × 26 cm. Price \$10.50.

This installment of over 600 large pages of Guertler's Text and Handbook of the Constitution and the Physical, Chemical and Technical Properties of the Metals and Metallic Alloys is the third section of the first part of the second volume! It aims to cover completely this particular subdivision of human knowledge, and indeed appears to do so with reasonable success.

The first section of 30 pages contains a general introduction dealing with the potentials exhibited by the pure metals, and follows the usual mode of presentation. The second section of over 400 pages, the *pièce de résistance* of the book, contains in systematic form all the existing information regarding the potentials of metallic alloys. Binary mixtures come first, followed by the ternary and polynary. Of particular interest is the summary of our present knowledge regarding the potentials of the amalgams, and the electrochemical behavior of the various sorts of iron.

The third section deals with the preparation of metallic alloys by precipitation; the fourth with the processes taking place during the electrolysis of solutions of metallic salts. In this section there is a short, but thorough discussion of polarization, overvoltage, the form of electrically deposited metals, and the production of alloys by electrical deposition, both from aqueous solutions, and from fused salts. The final (fifth) section deals with the anodic behavior of metals and metallic alloys.

The book is carefully, clearly and succinctly written. It appears to bring the various subjects right up to date, as references to the 1921 literature are frequent. Moreover, it is replete with references to the work of non-German, and particularly of American, investigators. The paper and printing are excellent.

The only serious flaw which the reviewer has noted is the method adopted for references to the original literature. Only the name of the investigator and the year are given. There is no mention of the name of the article, nor of the name of the journal in which it appeared. The editor of the Handbook as a whole (Guertler) alleges (1) that these references are adequate, and (2) that any other method would have been prohibitive in cost. The first statement shows an almost inexcusable disregard for the time and convenience of the reader, and hence a miscon-

ception of the function of a scientific publication of this kind. As regards the second statement, the number of references per page is not by any means unusually large, surely no greater than in an ordinary Journal article. An explanation of this peculiar procedure, but hardly a satisfactory one, may be found in the announcement, after the preface, that an additional volume of the Handbook will be issued, called "A Reference Book to the Literature of the Science of Metals." ARTHUR B. LAMB

**The Vitamins.** By H. C. SHERMAN, Professor of Food Chemistry, Columbia University, and S. L. Smith, Specialist in Biological and Food Chemistry, United States Department of Agriculture. American Chemical Society Monograph Series. The Chemical Catalog Company, Inc., 1 Madison Avenue, New York, U. S. A., 1922. iii + 273 pp. 20 fig. 23.5 × 15 cm. Price \$4.00.

When it was announced that Professor Sherman was to prepare a monograph on the vitamins, we anticipated that we should be given an excellent review of this new subject, and we were not disappointed. As was to be expected from his experience as an investigator in the field of animal nutrition and from his experience as a book maker, the treatment of the subject is comprehensive, but delightfully conservative.

Professor Sherman and his colleague, Mr. S. L. Smith, have arranged the material in 5 chapters. Chapter 1 gives an historical sketch of vitamins which is the best we have seen. In the main, it depicts the development of the subject as it has actually taken place, and as the work of many individuals rather than the product of one or two minds, as some writers would have us believe. Then follow 3 chapters, each dealing with a particular vitamin, but recognizing the possibility of the composite nature of each class. Chapter 2 treats of vitamin B (the antineuritic vitamin), Chapter 3 of vitamin C (the antiscorbutic vitamin), and Chapter 4 of vitamin A (the fat soluble vitamin). In Chapter 5 there is a discussion of the distribution of the vitamins in natural foods so far as they have been investigated. This chapter has particular value for dietitians and medical men.

An extensive bibliography is added which makes the monograph of very great value and guarantees its wide use not only by those curious only about vitamins, but by investigators in this field. The closing paragraph to Chapter 5 is worth repeating, as the exploitation of special materials for their vitamin content is unjustifiable in a properly selected dietary.

"Even with our present knowledge we believe it safe to say that with a dietary selected to make the best use of our ordinary staple foods there will be rarely if ever occasion to purchase vitamins in any other form, or to give any greater anxiety to the vitamins than to some other factors which enter into our present conception of nutritive requirements and food values."

E. B. HART

# THE JOURNAL

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[CONTRIBUTION FROM THE HAVEMEYER CHEMICAL LABORATORY, NEW YORK  
UNIVERSITY]

## THE SYSTEM, SILVER PERCHLORATE-WATER-BENZENE

BY ARTHUR E. HILL

Received November 1, 1921

### Introduction

In a previous communication<sup>1</sup> attention was called to the fact that silver perchlorate has a moderate solubility in benzene, and that the addition of about 1% of water to a complex of salt and saturated solution causes the formation of two liquid phases, each high in benzene but differing in water content and salt content; under certain conditions a third liquid phase is obtained.<sup>2</sup> This ternary system has now been studied from the temperature of the ternary eutectic up to the boiling points of the liquids and in some cases beyond the boiling points. Two compounds have been found, a hydrate of the formula  $\text{AgClO}_4 \cdot \text{H}_2\text{O}$  and a benzene addition compound of the formula  $\text{AgClO}_4 \cdot \text{C}_6\text{H}_6$ ; these two solids, together with the anhydrous salt, benzene, ice, the three liquids and the vapor, give rise to a very considerable number of invariant points and 4-phase equilibria which have been studied. A complete representation of the 3-component system, from its lowest eutectic temperature up to the melting point of the silver perchlorate, is given in the following pages.

<sup>1</sup> Hill, *THIS JOURNAL*, 43, 254 (1921).

<sup>2</sup> Professor E. W. Washburn of the University of Illinois made a prior observation of the occurrence of 3 liquid phases in this system, the work being embodied in a Bachelor's thesis presented at that institution by Mr. Russel W. Millar in 1916. Professor Washburn has very courteously left the matter to me for complete investigation.

### The Three Binary Systems

Study was made of each of the 3 binary systems from which the ternary system is composed. In the system, silver perchlorate and water, solubility determinations have been made from 100° downward to the binary eutectic, the concentration of salt being determined through direct titration by Volhard's method; freezing-point determinations, made by use of the Beckmann apparatus, were carried out to complete the curve from the eutectic to the water axis. The low temperatures required were obtained by use of a cooling bath of solid carbon dioxide and ether.

It was found that the hydrate  $\text{AgClO}_4 \cdot \text{H}_2\text{O}$  is stable up to 43°. The transition point was determined by cooling-point curves, and agrees well with that indicated by the solubility curves given below in Fig. 1. The formation of a hydrate was proved by the observation of a small rise in temperature upon addition of a small amount of water (about 9%) to a quantity of anhydrous salt; the relatively small rise in temperature which was noted indicates qualitatively that the heat of formation is small. The composition of the hydrate was determined by draining crystals at room temperature and drying them over anhydrous silver perchlorate in a very small desiccator; such a system should give a vapor tension in equilibrium with the hydrate.<sup>3</sup> The analysis showed 90.68% and 90.96% of silver perchlorate present, as against 92.00% required by the formula  $\text{AgClO}_4 \cdot \text{H}_2\text{O}$ ; the retention of about 1% of water by the crystals is not surprising in view of their very hygroscopic character. The solubility figures are given in Table I.

TABLE I  
SILVER PERCHLORATE AND WATER

Solid phase	Temp. °C.	Density	$\text{AgClO}_4$ , % by wt.	$\text{H}_2\text{O}$ , % by wt.
$\text{AgClO}_4$ .....	480	...	100.00	..
	99	3.069	88.8	11.2
	75	3.022	88.1	11.9
$(\text{AgClO}_4 \cdot \text{H}_2\text{O}(\text{metastable}))$ ....	50	2.995	87.2	12.8
$\text{AgClO}_4 + \text{AgClO}_4 \cdot \text{H}_2\text{O}$ .....	43	...	86.5	13.5
$\text{AgClO}_4 \cdot \text{H}_2\text{O}$ .....	25	2.806	84.5	15.5
$\text{AgClO}_4 \cdot \text{H}_2\text{O}$ .....	0	2.667	81.3	18.7
$\text{AgClO}_4 \cdot \text{H}_2\text{O} + \text{Ice}$ .....	-58.2	2.315	73.9	26.1
Ice.....	-40	...	70.4	29.6
	-24	...	60.3	39.7
	-10	...	45.2	54.8
	-3	...	26.55	73.45
	-0.16	...	0.96	99.04
	0.0	...	0.00	100.0
	0.0	...	0.00	100.0

The eutectic temperature, -58.2°, is lower than that of any other true salt in water, and only in the cases of hydrogen chloride in water, po-

<sup>3</sup> Hill, *THIS JOURNAL*, **44**, 546 (1922).

tassium hydroxide in water, and sulfuric acid in water have lower eutectics been found. The solubility of the salt in water is exceedingly high, and the curve, shown in Fig. 1, is made up of two practically straight lines, leading to the melting point of the salt,  $480^{\circ}$ .<sup>4</sup> The freezing-point determinations at low concentrations of the salt show it to be normally dissociated in water (81.5% at 0.047 *N*).

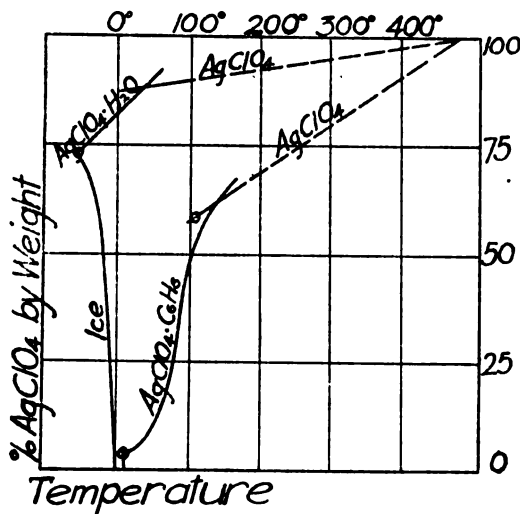


Fig. 1.—Solubility of  $\text{AgClO}_4$  in  $\text{H}_2\text{O}$  (upper curve);  $\text{AgClO}_4$  in  $\text{C}_6\text{H}_6$  (lower curve).

In determining the solubility curve of the salt in benzene, solutions saturated at temperatures from  $25^{\circ}$  to  $80^{\circ}$  were pipetted into flasks and, after weighing, treated with water to extract the silver salt, which was then titrated with standard thiocyanate solution. The determinations at temperatures above  $80^{\circ}$  were made by sealing weighed amounts of silver perchlorate and benzene in small glass tubes, which were rocked mechanically in a large heating bath of calcium chloride solution in which the temperature was slowly raised; the temperature at which the solid disappeared was taken as corresponding to a saturated solution of the composition taken. The benzene used was purified as noted later, and the cryoscopic determinations made in the usual Beckmann apparatus.

The compound  $\text{AgClO}_4 \cdot \text{C}_6\text{H}_6$  was found to be the solid phase at all ordinary temperatures. Crystals formed from benzene solution and dried over anhydrous silver perchlorate were found upon analysis to contain 72.14% of  $\text{AgClO}_4$ ; calculated from the formula, 72.64%. Attempts to determine the transition temperature of the double compound showed it to be surprisingly high; on being heated in sealed tubes, the compound

<sup>4</sup> Carnelly, *J. Chem. Soc.*, 45, 409 (1884).

showed partial liquefaction at 140° to 146°. From the solubility measurements given in Table II it appears that the transition temperature is about 145°, over 60° above the boiling point of benzene.

TABLE II  
SILVER PERCHLORATE AND BENZENE

Solid phase	Temp. °C.	Density	AgClO <sub>4</sub> % by wt.	H <sub>2</sub> O% by wt.
AgClO <sub>4</sub> .....	480	...	100.0	..
	(over 160)	...	65.6	34.4
	159	...	64.6	35.4
AgClO <sub>4</sub> + AgClO <sub>4</sub> .C <sub>6</sub> H <sub>6</sub> .....	145	...	63.0	37.0
AgClO <sub>4</sub> (metastable).....	140	...	62.6	37.4
AgClO <sub>4</sub> .C <sub>6</sub> H <sub>6</sub> .....	138.5	...	60.0	40.0
	115.5	...	50.5	49.5
	92	...	40.1	59.9
	80.3	1.164	32.2	67.8
	50	0.895	10.07	89.93
	25	0.906	5.00	95.00
AgClO <sub>4</sub> .C <sub>6</sub> H <sub>6</sub> + C <sub>6</sub> H <sub>6</sub> .....	5.12	0.909	3.44	96.56
C <sub>6</sub> H <sub>6</sub> .....	5.48	...	0.00	100.00

The salt is associated in benzene solution as molecules of double and triple the normal molecular weight, in equilibrium with unassociated molecules; electrolytic dissociation does not occur.<sup>5</sup> This considerable association explains the fact that the eutectic temperature (5.12°) is but slightly lower than the freezing point of pure benzene, 5.48°.<sup>6</sup> The solubility curve rising from the eutectic (Fig. 1), becomes very steep at temperatures above 50°, flattening out again at higher temperatures, and showing a distinct double flexure. The form of the curve is very similar to that observed for salicylic acid and water by Alexejew,<sup>7</sup> in which case the formation of two liquid phases was observed in the metastable region to the left of the solubility curve. In the case of silver perchlorate and benzene, the formation of two liquids was not observed upon undercooling the solutions as much as 30°, but it is evident from the nearly perpendicular character of the curve that changes occur in the solution of the kind which frequently produce 2 liquid phases, which are in the stable region when the solubility curve is perpendicular or inclined toward the vertical axis with increasing concentration, or in the metastable region when the solubility curve does not quite reach the perpendicular. This approach of the curve to a condition demanding 2 liquid phases will be referred to later as explaining in part the occurrence, in the 3-component system including water, of one more liquid phase than would be anticipated from the facts as to the 2-component systems.

<sup>5</sup> Hill, *THIS JOURNAL*, 43, 258 (1921).

<sup>6</sup> Richards and Shipley, *ibid.*, 41, 2002 (1919).

<sup>7</sup> Alexejew, *Wied. Ann.*, 28, 330 (1886).

For the system, benzene-water, a complete investigation has not yet been made. Herz<sup>8</sup> gives the solubility of water in benzene as 0.21% at 22°, from which value Richards and Shipley<sup>9</sup> dissent on the basis of freezing-point determinations made by them, which give by calculation a solubility of about 0.03% at 5.4° if a normal molecular weight is assigned to water. Three determinations made in the course of my work give 0.077° as the average depression, which is in fair agreement with Richards and Shipley's more carefully determined figure 0.09°. This places the quadruple point at about 5.40°. Clifford<sup>9</sup> has recently obtained, by displacing the water from saturated benzene solutions and weighing the water obtained, figures rising from 0.046% at 21° to 0.113% at 55°, which are a little higher than those of Richards and Shipley; Groschuff has a slightly higher set of figures. By an accurate method described later in this report, a value of 0.06% for the solubility of water in benzene at 25° has been obtained. A careful investigation of this solubility curve is now being conducted in this Laboratory, but it has not appeared necessary to delay this publication until the completion of that work.

For the solubility of benzene in water we have Herz's<sup>8</sup> figure of 0.08% at 22°. Three determinations of the freezing point of water saturated with benzene have given me an average value of 0.037° for the depression, which by calculation gives a benzene concentration of 0.153% at 0°. The upper and lower sections of the solubility curve are, therefore, still open to question; however it appears clear that the mutual solubilities are very low, as indicated in Fig. 2. From the information at hand we should have to deduce that the solubility of water in benzene increases with rising temperature, and that of benzene in water decreases under the same change of conditions.

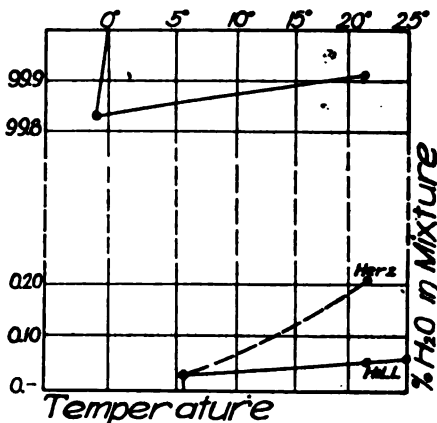


Fig. 2.—Solubility of water and benzene.

### The Ternary System

**Methods of Experimentation.**—In the analysis of solutions containing the 3 components the silver perchlorate has been determined directly by titration with standard ammonium thiocyanate. No suitable direct method could be found for determining the water or the benzene. The

<sup>8</sup> Herz, *Ber.*, 31, 2669 (1898).

<sup>9</sup> Clifford, *J. Ind. Eng. Chem.*, 13, 632 (1921). Groschuff, *Z. Elektrochem.*, 17, 348 (1911).



indirect method adopted consists in preparing samples of benzene and water by weighing each of them into a cylinder and using this mixed solvent to determine the solubility of silver perchlorate at  $25^{\circ}$  in an accurately controlled thermostat; the figures thus obtained, which are given later in Table IV, were plotted so as to give a solubility curve which could be used for reference purposes. The solution obtained in any experiment at any temperature, after determination of its silver perchlorate concentration, was pipetted into a dry cylinder, weighed, treated with excess of anhydrous salt, and agitated at  $25^{\circ}$  until equilibrium was reached; a sample was titrated for its new content of silver perchlorate, and the point corresponding to this composition on the  $25^{\circ}$  solubility curve was taken as giving the relative proportions of water and benzene present. This method gives very accurate results in all mixtures except those in which the benzene concentration is below 2%; in these latter cases the solubility curve at  $25^{\circ}$  is not suited to give accurate readings, since it is almost parallel to the water-benzene axis.

The solid phase present, when its composition was not obvious, was determined by application of phase-rule principles; a complex of salt, water and benzene having given a solution of a certain composition, it follows that a straight line connecting these two points, on the triangular diagram described below, leads to the composition of the solid phase, which, as all the solid phases are either binary compounds or of a single component, is found upon one of the sides of the triangle.

The benzene and silver perchlorate used were carefully purified. The benzene was washed with conc. sulfuric acid and then with water, dried with calcium chloride, then recrystallized, and finally dried and kept over metallic sodium. The principal sample used showed a melting point of  $5.432^{\circ}$  which is  $0.048^{\circ}$  lower than Richards' quoted figure of  $5.48^{\circ}$ . All measurements of temperature involving solid benzene have been corrected by  $0.048^{\circ}$  to agree with Richards' data. The silver perchlorate used was prepared from silver nitrate by precipitation with sodium hydroxide; the precipitated silver hydroxide after washing was then dissolved in 60% perchloric acid and the solution evaporated on the water-bath to partial crystallization. The mixture was allowed to cool and was filtered at a temperature above  $43^{\circ}$ , to avoid formation of the hydrate; the crystals were then centrifuged and dried in an electric oven at  $105^{\circ}$  to  $110^{\circ}$  for several days before use, on account of their extremely hygroscopic character. Various samples showed upon analysis a purity of 99.6% to 99.8%, determined by titration with standard thiocyanate solution.

Solubility determinations at temperatures other than  $25^{\circ}$  were made in ordinary Beckmann freezing-point tubes, immersed in a large volume of water at the desired temperature and stirred until equilibrium was reached. The various invariant temperatures were determined in the same apparatus. Thermometers were calibrated at the freezing point and boiling point of pure water and in solid carbon dioxide, which was assumed to be at  $-78^{\circ}$ .

The composition of the various phases has been represented in weight per cent. on the familiar triangular diagram; the vertex representing pure silver perchlorate is indicated by the letter S, that for water by W and

that for benzene by B. The composition of any point within the triangle shows the percentage of salt, water and benzene by its perpendicular distance from the sides opposite to S, W and B respectively. In the diagrams following, the compositions are indicated approximately, and not according to accurate scale, since many points fall so close to the sides of the triangle as to make their correct representation on a small scale confusing to the reader.

**The Invariant Equilibria and the Monovariant Equilibria.**—Since the gaseous phase is present in all the experiments made, 4 additional phases are necessary to define an invariant equilibrium, or 3 to define a monovariant equilibrium. With 5 solid phases possible and 3 liquids, the number of such equilibria possible is naturally very large. These are of course not all realizable, but the astonishing thing is that so large a number of them are actually met with in this system. For convenience in study, a list of such equilibria realized and studied is given in Table III. The symbol  $S_H$  is used for the hydrate  $AgClO_4 \cdot H_2O$ ,  $S_B$  for the compound  $AgClO_4 \cdot C_6H_6$ , S, W, and B for solid salt, ice and benzene, and  $L_3$ ,  $L_2$  and  $L_1$  for the 3 liquid phases. The numbers and letters assigned to the various equilibria will be used in the discussion later.

TABLE III  
INVARIANT AND MONOVARIENT EQUILIBRIA

Quintuple Point

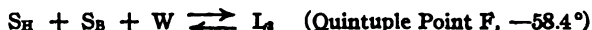
F	°C.	$S_H + W + S_B + L_3$
E	-58.4	$W + S_B + B + L_3$
D	-57.8	$S_B + B + L_3 + L_2$
C	-2.7	$S_B + B + L_2 + L_1$
B	+4.98	$B + L_3 + L_2 + L_1$
A	+5.24	$S_H + S_B + S + L_3$
Equilibrium		
	+42.1	
	24	$S_H + W + S_B$
	23	$S_H + W + L_3$
	22 (3)	$S_H + S_B + L_3$
	21 (20)	$W + S_B + L_3$
	19	$W + S_B + B$
	18	$W + B + L_3$
	17 (16)	$S_B + B + L_3$
	15 (12)	$S_B + B + L_2$
	14	$S_B + L_3 + L_2$
	13 (8)	$B + L_3 + L_2$
	11	$S_B + B + L_1$
	10	$S_B + L_2 + L_1$
	9 (7)	$B + L_2 + L_1$
	6	$B + L_3 + L_1$
	5	$L_2 + L_3 + L_1$
	4	$S_H + S_B + S$
	2	$S_H + S + L_3$
	1	$S_B + S + L_3$

In addition to these 6 invariant and 18 monovariant equilibria, there are 17 divariant equilibria which have been studied (two phases and vapor), and 8 trivariant equilibria (1 phase and vapor); these latter have been realized but not studied. The total number of equilibria existing in this 3-component system is therefore 49.

In order to represent these equilibria a triangular prism can be used. The space figure obtained, however, is too complicated for simple graphic representation. For that reason it seems best to follow the method used by Schreinemakers,<sup>10</sup> in which the various invariant and monovariant equilibria are shown by their projection upon the base of a triangular prism (Fig. 3), and the changes of the system with varying temperature are shown by isothermal cross-sections at suitable temperatures (Figs. 4 to 21).

The eutectic for the complete system was found to lie at  $-58.4^\circ$ , which temperature is represented as Quintuple Point F in Fig. 3. The liquid phase appearing here is low in benzene, and the composition not widely different from that at the eutectic temperature for silver perchlorate and water alone,  $-58.2^\circ$  (Table I). A second quintuple point was found at a temperature only slightly higher than that of Quintuple Point F, namely at  $-57.8^\circ$ . It was assured by the low temperature and the composition of the liquid phases at the point F that ice and the hydrate  $\text{AgClO}_4 \cdot \text{H}_2\text{O}$  were present as solid phases, but the third solid phase could not be directly determined. The point was settled by approaching the quintuple point from mixtures of different total composition. When a phase complex was used which gave the equilibrium  $S_H + S_B + I_4$  (Equil. 22) the quintuple point of lower temperature was found. When the equilibrium  $W + B + I_4$  (Equil. 18) was used as the path of approach, the higher quintuple point was found. This established that  $S_B$  is the third solid phase both at Quintuple Point F, and at E also. At Quintuple Point F ( $-58.4^\circ$ ) the liquid phase was found by analysis to contain 72.97% of silver perchlorate. The benzene content could not be determined by the method previously outlined, though it was found to be less than 1.6%.

With the composition of the solid and liquid phases determined, it is possible to write the phase reaction which occurs; using the system of notation previously outlined, it becomes,



in which the change upon addition of heat is written from left to right. At this temperature there begin 4 monovariant equilibria, of which 1 exists at lower temperatures and 3 exist at higher temperatures. These may be designated as follows.

<sup>10</sup> Schreinemakers, *Z. physik. Chem.*, 25, 543 (1898).

		Equil.
At lower temperatures.....	$S_H + W + S_B$	24
At higher temperatures.....	$S_H + W + L_A$	23
At higher temperatures.....	$S_H + S_B + L_A$	22
At higher temperatures.....	$W + S_B + L_A$	21

In Fig. 3, the approximate position of the quintuple point has been represented by F, and the 3 equilibria at higher temperatures by the lines Fh, FA and FE.

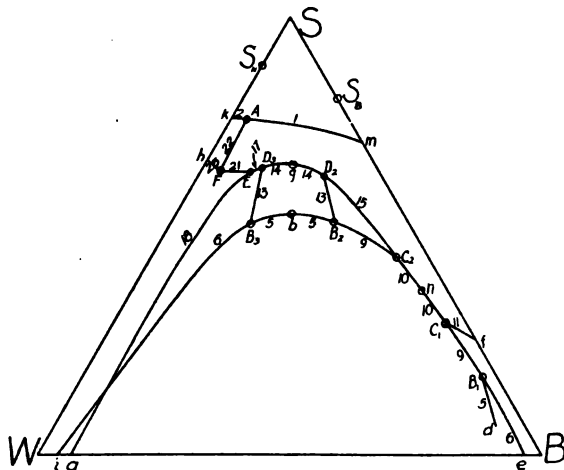


Fig. 3.—Monovariant equilibria (4-phase) in the system,  $\text{AgClO}_4\text{-C}_6\text{H}_6\text{-H}_2\text{O}$ .

Equilibrium 24 represents the three solid phases  $S_H$ ,  $S_B$  and ice (W) in contact with vapor, of which only the latter is capable of varying in composition. Measurements of vapor tension have not been made in the study of this system. Equilibrium 23, in which  $S_H$ , W, and  $L_A$  are present, exists only over a short temperature range, during which the benzene content  $L_A$  drops from an initially small value to zero; that is, the equilibrium ends at the binary eutectic for salt and pure water, at  $-58.2^\circ$ . The composition of  $L_A$  at these two points is given below, the benzene content being estimated.

	Equilibrium 23.	$(S_H + W + L_A)$			
	Temp. $^\circ\text{C}$ .	$\text{AgClO}_4$ %	$\text{C}_6\text{H}_6$ %	$\text{H}_2\text{O}$ %	Density
F.....	-58.4	72.97	(0.5)	26.53	...
h.....	-58.2	73.98	0.0	26.02	2.345

Equilibrium 22 (hydrate, benzene-compound and solution) exists over a long range of temperature, from  $-58.4$  to  $+42.1^\circ$ , at which latter temperature (Quintuple Point A) the hydrate changes to anhydrous salt and solution. During this rise of temperature there is of course a gradual increase in the salt concentration of the solution, but the benzene

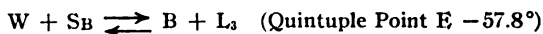
concentration is always low, as represented schematically by the line FA. Since this solubility curve presumably parallels very closely the solubility curve of the hydrate in pure water (Table I), it was not thought worth while to make analyses at intermediate temperatures. The composition of  $L_3$  at the extreme temperatures for this equilibrium is as follows.

Equilibrium 22 (3). ( $S_H + S_B + L_3$ )					
	Temp. °C.	AgClO <sub>4</sub> %	C <sub>6</sub> H <sub>6</sub> %	H <sub>2</sub> O %	Density
F.....	-58.4	72.97	(0.50)	26.53	...
A.....	+42.1	87.12	0.70	12.18	2.956

The remaining monovariant equilibrium beginning at the eutectic is Equilibrium 21 ( $W + S_B + L_3$ ), which exists over but a short range of temperature, coming to an end with the precipitation of an additional phase, solid benzene, at the invariant temperature  $-57.8^\circ$ . The change in composition, with respect to silver perchlorate, is very slight, and the change in benzene concentration is likewise small. It will be remembered that all benzene concentrations found to be less than 1.6% are given only as estimated amounts.

Equilibrium 21 (20). ( $W + S_B + L_3$ )				
	Temp. °C.	AgClO <sub>4</sub> %	C <sub>6</sub> H <sub>6</sub> %	H <sub>2</sub> O %
F.....	-58.4	72.97	(0.50)	26.53
E.....	-57.8	72.85	(1.00)	26.15

At the new invariant temperature (Quintuple Point E) the composition of the liquid phase is as given immediately above. The appearance of solid benzene from a system consisting of ice, solvate and solution, as represented by the points W,  $S_B$  and F in Fig. 3, which do not include the point B in the triangle joining them, can be expressed only by the following phase reaction



and the monovariant equilibria beginning here are

		Equil.
At lower temperatures.....	$W + S_B + L_3$	20 = 21
	$W + S_B + B$	19
At higher temperatures.....	$W + B + L_3$	18
	$S_B + B + L_3$	17 = 16

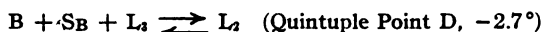
The two equilibria existing at lower temperatures require no discussion, as Equilibrium 20 is of course the same as Equilibrium 21, while Equilibrium 19 contains no phase of variable composition except vapor. Equilibrium 18 exists over a long temperature rise, and is represented by the line Ea, which runs close to the SW axis (*i. e.*, there is but little benzene in the solution) and terminates at the eutectic a on the water-benzene axis, which is at  $0.037^\circ$ . Analyses were made at several temperatures.

Equilibrium 18. (W + B + L <sub>3</sub> )				
	Temp. °C.	AgClO <sub>4</sub> %	C <sub>6</sub> H <sub>6</sub> %	H <sub>2</sub> O %
E.....	-57.8	72.85	(1.00)	26.15
	-50	70.31	(0.90)	28.79
	-7	33.3	(0.30)	66.4
a.....	-0.037	0.0	0.153	99.84
				1.376

Equilibrium 17, represented by the line ED<sub>3</sub>, represents the solution in contact with S<sub>B</sub> and solid benzene (B), which condition can exist over more than 50° range, ending with the formation of a new liquid phase at -2.7°. This constitutes a new quintuple point having two liquid phases present, represented by D<sub>3</sub> and D<sub>2</sub>. The analyses of L<sub>3</sub> are given below.

Equilibrium 17(16). (S <sub>B</sub> + B + L <sub>3</sub> )				
	Temp. °C.	AgClO <sub>4</sub> %	C <sub>6</sub> H <sub>6</sub> %	H <sub>2</sub> O %
E.....	-57.8	72.85	(1.00)	26.15
	-18	72.39	2.20	25.41
D <sub>3</sub> .....	-2.7	72.18	4.34	23.48
				2.243

It will be seen that during rise in temperature there is no substantial change in the salt content of the solution L<sub>3</sub> but that the liquid takes up benzene rapidly, so that its composition comes into the region where accurate analyses are possible. The new liquid L<sub>2</sub>, having its origin at the invariant temperature -2.7°, is represented by the point D<sub>2</sub> in Fig. 3, and is widely different in composition from L<sub>3</sub>. Its composition falls within a triangle drawn connecting the points D<sub>3</sub>, S<sub>B</sub> and B, from which it follows that L<sub>2</sub> is produced by reaction of the other three phases.



	AgClO <sub>4</sub> %	C <sub>6</sub> H <sub>6</sub> %	H <sub>2</sub> O %	Density
Composition L <sub>3</sub>	72.18	4.34	23.48	2.243
L <sub>2</sub>	54.36	37.32	8.32	1.644

At Quintuple Point D there originate four monovariant equilibria.

	Equil.
At lower temperatures.....	S <sub>B</sub> + B + L <sub>3</sub> 16 = 17
	S <sub>B</sub> + B + L <sub>2</sub> 15
At higher temperatures.....	S <sub>B</sub> + L <sub>3</sub> + L <sub>2</sub> 14
	B + L <sub>3</sub> + L <sub>2</sub> 13

Of these, Equilibrium 16 is of course the same as 17, which has already been discussed. Equilibrium 14 represents the compound S<sub>B</sub> in contact with the two saturated solutions, L<sub>3</sub> and L<sub>2</sub>. As the temperature of this system is raised, L<sub>3</sub> is found to decrease in salt concentration and in water concentration, while L<sub>2</sub> undergoes exactly the opposite changes. The two liquids are therefore approaching each other in composition, and at some temperature will become consolute. The consolute temperature was

easily determined to be  $10.4^{\circ}$ ; as the 2 liquids are stirred in contact with excess salt and with slowly rising temperature, the emulsion which is seen at lower temperatures passes at  $10.4^{\circ}$  into the critical opalescence<sup>11</sup> which is characteristic of the coalescence of 2 liquids. The phenomenon is less sharply marked with falling temperatures, since in the latter case the precipitation of excess salt interferes with the observation of the changes in the liquid phases. The changes in composition are indicated in Fig. 3 by the 2 lines  $D_3g$  and  $D_2g$  and were found by analysis to be as follows.

Equilibrium 14. ( $S_B + L_3 + L_2$ )

	Temp. °C.	$AgClO_4$ %	$C_6H_6$ %	$H_2O$ %	Density
$D_3$	- 2.7	$L_3$ .....72.18	4.34	23.48	2.244
$D_2$		$L_2$ .....54.36	37.32	8.32	1.644
$g$	+10.4	$L_3 = L_2$ .....64.02	22.72	13.26	1.876

Equilibrium 13 (benzene,  $L_3$  and  $L_2$ ) also includes 2 liquid phases of variable composition. As the temperature rises, each liquid becomes lower in salt concentration, with small changes in concentration of benzene and water, until at  $5.24^{\circ}$  a third liquid phase ( $L_1$ ) appears. This is, however, not the next quintuple point in order, but is one occurring at a higher temperature, and will be discussed as Quintuple Point B a little later. The composition at the beginning and ending of this equilibrium has been determined: in Fig. 3 the two lines  $D_1B_1$  and  $D_2B_1$  represent the same.

Equilibrium 13 (8). ( $B + L_3 + L_2$ )

	Temp. °C.	$AgClO_4$ %	$C_6H_6$ %	$H_2O$ %	Density
$D_3$	-2.7	$L_3$ .....72.18	4.34	23.48	2.244
$D_2$		$L_2$ .....54.36	37.32	8.32	1.644
$B_1$	5.24	$L_3$ .....70.30	1.60	28.1	2.141
$B_2$		$L_2$ .....52.02	35.30	12.68	1.532

Equilibrium 15 represents solution  $L_2$  in contact with the compound  $S_B$  and with solid benzene. It may be viewed as the continuation of Equilibria 18, 17 and 14, and will eventually terminate in the binary eutectic for salt and benzene at  $f$ ; but its progress is again interrupted by the appearance of another liquid phase, which has already been referred to as  $L_1$ . This third liquid contains but little salt and its water content is never more than a very few tenths of 1%. The appearance of this phase occasions another quintuple point (C) at a temperature of  $4.98^{\circ}$ . It is to be noted that although 3 liquid phases are existent at this temperature, they are not coexistent; the 2 coexistent liquids at the quintuple point are  $L_2$  and  $L_1$ , both relatively low in water; if the water concentration is increased at this temperature  $L_1$  and the compound

<sup>11</sup> Rothmund, *Z. physik Chem.*, 26, 446 (1898). Ostwald, "Lehrbuch der allgemeinen Chemie," (2nd Edition), W. Engelmann, Leipsic, 1903, II, 2, 648.

$S_B$  will eventually disappear and  $L_3$  will appear, giving the monovariant Equilibrium 13. This will be apparent in the isotherm for  $4.98^\circ$ , given later. The data for Equilibrium 15 are as follows, and are represented by the curve  $D_2C_2$  in Fig. 3.

Equilibrium 15 (12). ( $S_B + B + L_2$ )					
	Temp. °C.	$AgClO_4$ %	$C_6H_6$ %	$H_2O$ %	Density
$D_1$ .....	-2.7	54.36	37.32	8.22	1.644
$C_2$ .....	+4.98	36.86	61.38	1.76	1.276

It is to be noted that with moderate change in water concentration there is relatively large change in salt and benzene concentration, which will be found true of all equilibria represented by points approaching the benzene vertex; both solubility curves and distribution curves in this part of the diagram run nearly parallel to the axis  $S_B$ .

At the temperature  $+4.98^\circ$  the new Quintuple Point C appears. The composition of the liquid phases is as follows.

		$AgClO_4$ %	$C_6H_6$ %	$H_2O$ %	Density
$C_2$ .....	$L_2$	36.86	61.38	1.76	1.276
$C_1$ .....	$L_1$	5.03	94.71	0.20	0.923

On plotting to scale the positions of the 2 liquid phases and the 2 solid phases  $S_B$  and B it appears that  $L_1$  (represented in Fig. 3 by  $C_1$ ) falls within the triangle made by the other three, whence the phase reaction is the following.



and the 4 monovariant equilibria are

		Equil.
At lower temperatures.....	$S + B + L_2$	12 = 15
At higher temperatures.....	$S_B + B + L_1$	11
	$S_B + L_2 + L_1$	10
	$B + L_2 + L_1$	9 = 7

Equilibrium 12 is the same as 15, previously discussed. Equilibrium 10 is, like 14, marked by the approach of the two liquid phases toward the same composition as the temperature rises, but it has not been found possible to determine the consolute temperature. It is at least slightly higher than  $25^\circ$ , as will be shown in the discussion of the isotherm at that temperature, but the tendency of the 2 liquids to form very permanent emulsions is displayed for several degrees lower: the opalescence which appears and disappears promptly in the cases of Equilibria 14 and 5 when the consolute temperatures are reached, is found to exist over a wide temperature range in the case of the equilibrium being studied. From the fact that the solubility curve for silver perchlorate rises very sharply on the side of the benzene-salt axis with rise of temperature, it is safe to



estimate that this consolute temperature is not higher than  $30^\circ$ , which temperature will be adopted provisionally. Analyses of the solutions have been made, which are represented in Fig. 3 by the two lines  $C_2n$  and  $C_1n$ .

Equilibrium 10. ( $S_B + L_2 + L_1$ )

	Temp. °C.		AgClO <sub>4</sub> %	C <sub>6</sub> H <sub>6</sub> %	H <sub>2</sub> O %	Density
$C_2$ .....	4.98	$L_2$	36.86	61.38	1.76	1.276
$C_1$ .....		$L_1$	5.03	94.71	0.20	0.923
	25.00	$L_2$	31.92	67.03	1.04	1.200
		$L_1$	10.45	89.34	0.21	0.960
$n$ .....	(30.00)	$L_2 = L_1$	(25.00)	(74.0)	(1.00)	...

Equilibrium 11 shows the solution  $L_1$  in contact with solid benzene and the compound  $S_B$ . It has but a short temperature range, and ends with the disappearance of water from the liquid phase at the binary eutectic for salt and benzene, the temperature of which is  $5.12^\circ$ . It is thus to be looked upon as the prolongation of Equilibrium 10, which was the prolongation of Equilibria 15, 14 and 17, which latter had its origin at the ternary eutectic E,  $-57.8^\circ$ . The curve is shown as  $C_1f$  in Fig. 3, and the analyses are as follows.

Equilibrium 11. ( $S_B + B + L_1$ )

	Temp. °C.	AgClO <sub>4</sub> %	C <sub>6</sub> H <sub>6</sub> %	H <sub>2</sub> O %	Density
$C_1$ .....	4.98	5.03	94.77	0.20	0.923
$f$ .....	5.12	3.44	96.56	0.00	0.909

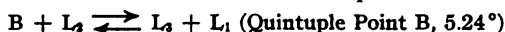
Equilibrium 9 (benzene,  $L_2$  and  $L_1$ ) continues with rising temperature to the point where, with increase in water and salt content in  $L_2$ , the liquid  $L_3$  appears, thus constituting the fifth quintuple point. The changes are represented in Fig. 3 by the two lines  $C_1B_1$  and  $C_2B_2$ , and the composition of the 2 liquid phases ( $L_2$  and  $L_1$ ) is given below, together with that of the third liquid,  $L_3$ , at the invariant temperature  $5.24^\circ$ .

Equilibrium 9 (7). ( $B + L_1 + L_2$ )

	Temp. °C.		AgClO <sub>4</sub> %	C <sub>6</sub> H <sub>6</sub> %	H <sub>2</sub> O %	Density
$C_1$ .....	4.98	$L_1$	5.03	94.77	0.20	0.923
$C_2$ .....		$L_2$	36.86	61.38	1.76	1.276
$B_1$ .....	5.24	$L_1$	1.72	98.20	0.077	0.896
$B_2$ .....		$L_2$	52.02	35.30	12.68	1.532
$B_3$ .....		$L_3$	70.30	(1.6)	28.1	2.141

At the new quintuple point,  $5.24^\circ$ , the 4 phases present (with vapor) are solid benzene,  $L_1$ ,  $L_2$ , and  $L_3$ . When the composition of these 4 phases as shown above is designated on the triangular diagram, no one of them appears within a triangle constructed upon the other 3; but a line connecting the benzene vertex with  $L_2$ , ( $B_2B$ ) crosses that connecting  $L_4$

and  $L_1(B_2B_1)$ , from which it follows that the phase reaction is as follows



The 4 monovariant equilibria arising at this temperature therefore occur in groups of 2 instead of groups of 1 and 3, and are as follows.

		Equil.
At lower temperatures.....	$B + L_2 + L_3$	8 = 13
	$B + L_2 + L_1$	7 = 9
At higher temperatures.....	$B + L_1 + L_3$	6
	$L_1 + L_2 + L_3$	5

It will be seen that Equilibrium 8 is the same as 13, arising at Quintuple Point D, and 7 is the same as 9, arising at Quintuple Point C, only the 2 equilibria which lead to higher temperatures being new. Equilibrium 6 ( $B + L_1 + L_3$ ) represents the freezing point of benzene in equilibrium with benzene-water solutions containing salt, and obviously must have its terminus at the freezing point of benzene in saturated water-benzene solutions free from salt, namely at  $5.40^\circ$ . The movement of the points representing the liquid phase is given in Fig. 3 by the two lines  $B_1e$  and  $B_3i$ , in which the point  $i$  is only very slightly to the left of  $a$ . The value for  $i$  is estimated from Fig. 2.

Equilibrium 6. ( $B + L_1 + L_3$ )						
	Temp. $^\circ\text{C}$		$\text{AgClO}_4$ %	$\text{C}_6\text{H}_6$ %	$\text{H}_2\text{O}$ %	Density
$B_1$ .....	5.24	$L_3$	70.33	(1.6)	28.1	2.141
$B_3$ .....		$L_1$	1.72	98.20	0.077	0.896
	5.30	$L_3$	70.24	(1.5)	28.26	2.151
		$L_1$	1.26	98.67	0.068	0.880
	5.367	$L_3$	67.7	(1.0)	31.3	...
		$L_1$	0.56	...	...	...
	5.392	$L_3$	48.4	(0.5)	51.1	1.643
		$L_1$	0.0	99.94	0.062	0.875
$i$ .....	5.40	$L_3$	0.0	(0.12)	99.88	...
$e$ .....		$L_1$	0.0	99.97	0.03 <sup>6</sup>	...

There is here an extremely large variation in the composition of  $L_3$  with a comparatively small change in  $L_1$ . This is in accord with the fact that the lines representing the 2 liquids are distribution curves, in which the amount of salt in the one is many thousand times that in the other; this ratio has been shown to be as high as 46000:1 at moderate concentrations.<sup>1</sup> The measurements of this distribution at  $25^\circ$  have been made at various concentrations and appear in Table V.

The equilibrium under discussion involves the melting point of a solid (benzene) in presence of a second liquid phase (water) and in presence of a third component (silver perchlorate) dissolved in the 2 liquids. The conditions governing such a transition point have been studied by Schreinemakers.<sup>12</sup> He arrives at the generalization that the

<sup>12</sup> Schreinemakers, *Z. physik. Chem.*, **25**, 305 (1898).

transition point of a solid in the presence of a second (liquid) component is raised by a third component if this latter is more soluble in the dilute than in the concentrated solution. In order to understand this generalization it is necessary to have in mind Schreinemakers' definition that the "dilute" solution is the solution containing the smaller amount of the solid component, and that solubility is the concentration of the third component per unit weight of the third plus the second, or liquid, component. With these definitions in mind, the theorem may be applied to the materials of Equilibrium 6, in which  $5.40^\circ$  is obviously the transition point of solid benzene in the presence of a second (liquid) component, water. This transition point should be raised or lowered by the third component, silver perchlorate, according as that substance is more soluble in the dilute (benzene-weak) solution or in the concentrated (benzene-rich) solution.  $L_3$  is obviously the dilute solution. The concentration of silver perchlorate in this phase at  $5.24^\circ$ , as defined above, is 70.33 divided by 70.33 plus 28.1 (expressed in grams) or 0.71, while in  $L_1$  it amounts to 1.72 divided by 1.72 plus 0.077, or 0.95; that is, it is higher in the concentrated solution  $L_1$ , whence it would follow that the transition temperature should be lowered by addition of silver perchlorate. Actually it is lowered from  $5.40^\circ$  to  $5.24^\circ$ , which accords with the requirements of the theorem. In this connection it may be stated that Schreinemakers' exceedingly valuable generalization would be much less liable to misinterpretation if it were phrased so as to consider solubility as the ratio of the third component to the first (or solid) component, in which case a rise in transition point would be required when the salt is more soluble in the concentrated solution.

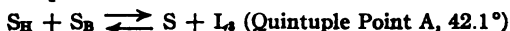
Equilibrium 5, remaining for discussion, is that in which 3 liquid phases coexist. It appears to be a novelty in 3-component systems, in that the other case studied by Schreinemakers,<sup>10</sup> namely, succinic nitrile, ether and water, is one in which all 3 pairs of components are partially miscible, giving at some temperature or temperatures 3 binodal curves, whose intersection gives rise to the isothermal invariant system of 3 liquids. In the case here found, however, water and benzene constitute the only pair of components giving 2 liquid phases and a binodal curve at any temperature known, either above or below the limits within which 3 liquid phases are found. A discussion of this phenomenon will be given later.

As the temperature rises, the composition of  $L_3$  and  $L_2$  in equilibrium with  $L_1$ , approaches the same value and at  $22.4^\circ$  the 2 phases in question coalesce. The temperature is in this case very sharply marked, and the point at which the emulsion gives place to the critical opalescence or the reverse, with rising or falling temperature, can be determined without error of more than  $0.1^\circ$ . If stirred above the temperature of  $22.4^\circ$

the system shows, in addition to the layer of  $L_1$  floating above, a single opalescent layer which retains its opalescent character as long as it contains any admixture of  $L_1$ ; below the consolute temperature,  $L_2$  and  $L_3$  separate into 2 perfectly clear and transparent phases in the course of a very few minutes. The compositions of the 3 liquids are given below, and the curves representing the direction of the changes are represented in Fig. 3 by the two lines  $B_2b$  and  $B_3b$ , meeting at the consolute point  $b$ , and the third line  $B_1d$ , ending at the concentration  $d$  at which the system ceases to be monovariant.

Equilibrium 5. ( $L_2 + L_3 + L_1$ )						
	Temp. °C.		$AgClO_4$ %	$C_6H_6$ %	$H_2O$ %	Density
$B_2$ .....	5.24	$L_2$	70.30	(1.6)	28.1	2.141
$B_3$ .....		$L_3$	52.02	35.30	12.68	1.532
$B_1$ .....		$L_1$	1.72	98.20	0.077	0.896
$b$ .....	22.4	$L_2 = L_3$	64.4	18.2	17.4	1.894
$d$ .....		$L_1$	1.57	98.32	0.09	0.884

The sixth and highest invariant temperature is  $42.1^\circ$  (Quintuple Point A). This quintuple point occurs as the result of a change in the monovariant system  $S_H + S_B + L_2$  (Equilibrium 22), which has its origin at the eutectic  $-58.4^\circ$  and continues over the interval of  $100^\circ$  with but slight change in composition of the liquid layers. It will be remembered that the transition point of the hydrate  $S_H$  is at  $+43.1^\circ$  (Table I) in the presence of water alone, from which it may be deduced that the presence of small amounts of the third component, benzene, will lower the temperature of its change into the anhydrous compound. By the use of cooling curves it was rather sharply determined that this change, in the presence of  $L_2$ , is at  $42.1^\circ$ , only a degree lower than the transition temperature in presence of pure water. The composition of the liquid phase  $L_2$  at this temperature falls outside the triangle joining  $S$ ,  $S_B$  and  $S_H$ , from which it follows that the phase reaction is



and the 4 equilibria are

	Equil.
At lower temperatures.....	4
	3 = 22
At higher temperatures.....	2
	1

Equilibrium 4 has no liquid phase, and Equilibrium 3 has been discussed. Equilibrium 2 exists over a range of only  $1^\circ$ , terminating at the transition point of the hydrate in presence of water.

Equilibrium 2. ( $S_H + S + L_2$ )					
	Temp. °C.	$AgClO_4$ %	$C_6H_6$ %	$H_2O$ %	Density
A.....	42.1	87.1	0.7	12.2	2.956
k.....	43.1	86.5	0.0	13.5	...

Equilibrium 1 also terminates at a transition point, that of the compound  $S_B$ , but the temperature range is over  $100^\circ$ , representing the large extent to which the transition point of the compound is lowered by the presence of water.

Equilibrium 1. ( $S_B + S + L_3$ )				
	Temp. °C.	$AgClO_4$ %	$C_6H_6$ %	$H_2O$ %
A.....	42.1	87.1	0.7	12.2
.....	100	84.4	7.3	8.3
m.....	145	63.0	37.0	0.0

Of the 24 equilibria originating at the 6 quintuple points, 3 have no phase of variable composition except vapor (24, 19, 4); 12 are denoted twice and represent 6 equilibria existing between quintuple points (22, 21, 17, 15, 13, 9); 3 terminate in the coalescence of 2 liquid phases at a consolute temperature (14, 10, 5); 4 end at the 3 binary eutectics and the quadruple point for benzene and water (23, 18, 11, 6), and the remaining 2 at the transition temperatures of the hydrate and the solid  $S_B$  (2, 1). Monovariant equilibria may, therefore, exist over the range of temperature between  $-58.4^\circ$  and  $145^\circ$ .

If the possibilities as to types of invariant and monovariant equilibria are noted, it will be found that the ternary system under discussion affords an instance of each. For invariant equilibria (vapor being assumed present), the three possibilities of type are  $SSSL$ ,  $SSL$ , and  $SLLL$ , where  $S$  denotes a solid phase and  $L$  a liquid; Quintuple Points F, E and A are of the first type, both C and D are of the second, and B is of the third. For univariant equilibria there are 4 possibilities, namely  $SSS$ ,  $SSL$ ,  $SL$ , and  $LLL$ , each of which is represented. The system affords at least one example of each general type of invariant or monovariant equilibrium possible for 3 components with 3 liquids.

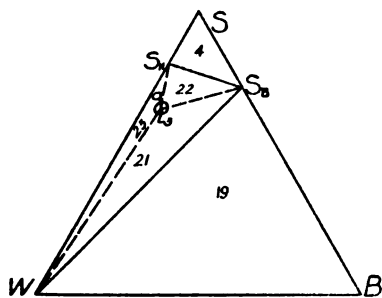
### The Isotherms

A study of the isotherms representing the ternary system shows an interesting gradual growth in complexity, beginning at the eutectic temperature and increasing up to a point between  $4.98^\circ$  and  $5.12^\circ$ , above which temperature conditions become gradually more and more simple until but few phase complexes are possible. These progressive changes will be shown in Figs. 4 to 21.

At temperatures below the eutectic,  $-58.4^\circ$ , there can exist only solid phases in equilibrium with vapor. When this temperature is reached, however, a liquid phase can exist, the composition of which is represented in Fig. 4 by the point a, quite close to the line  $SW$ , since the benzene content is very low. The triangles marked 4 and 19 represent monovariant equilibria involving no liquid, and may exist at temperatures below or above  $-58.4^\circ$ . The smaller triangles, 21, 22, and 23, repre-

sent equilibria originating at  $-58.4^{\circ}$  and continuing only at higher temperatures; if a phase complex of total composition falling within one of these triangles be prepared, it will fall into solution of the composition  $a$  and two solids represented by the other two angles of the triangle.

As the temperature is raised slightly above the quintuple point F, the area representing the solution  $L_3$  becomes larger, spreading out in all directions until at the temperature  $-58.2^\circ$  it touches the side SW, thus eliminating the triangle  $S_H + W + L_3$  and setting an upper limit to Equilibrium 23. Here the temperature at which the point a has reached the line SW represents of course the binary eutectic for salt and water. At slightly higher temperatures the liquid area takes the general form a b c d as shown in Fig. 5, retaining that shape until the temperature of Quintuple Point E is reached, at  $-57.8^\circ$ . Here the phase reaction previously discussed is the appearance of solid benzene as a new phase, causing the elimination of Equilibria 19 and 21 and the appearance of the 2 new equilibria, 17 and 18.



**Fig. 4.—Isotherm at  $-58.4^{\circ}$  (Quintuple Point F').**

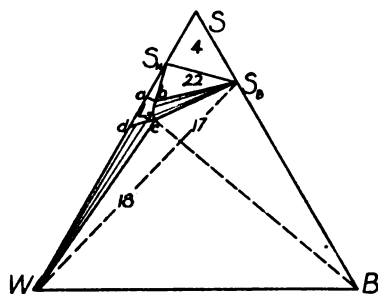
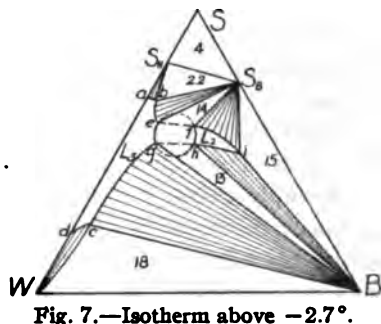
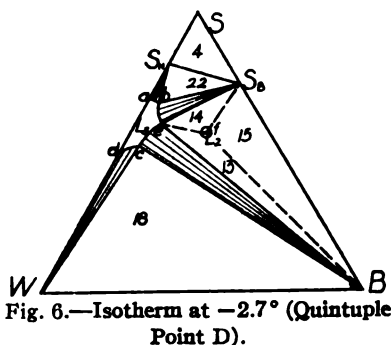


Fig. 5.—Isotherm at  $-57.8^{\circ}$  (Quintuple Point E).

As the temperature is further raised, there are but slight changes in this isotherm, which is in form the most persistent of the series; over a rise of about  $55^{\circ}$  the equilibria are those shown in Fig. 5, with the addition only of an area representing solid benzene in contact with  $L_3$ , which could be shown by the extension of the point c into a line acting as the base of this triangle. The general form of the area  $L_3$  is, therefore, that shown in Fig. 6: the analyses show that the area is small, and that it does not extend more than 1 or 2% in the direction of the benzene vertex until the next quintuple point is reached, at  $-2.7^{\circ}$ . At the point f is shown the approximate location of the newly appearing liquid phase,  $L_2$ , the formation of which brings Equilibrium 17 to an end and divides its area into those of the 3 equilibria 13, 14 and 15.

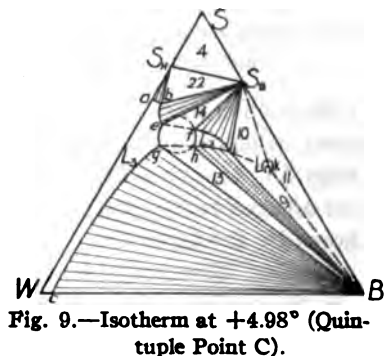
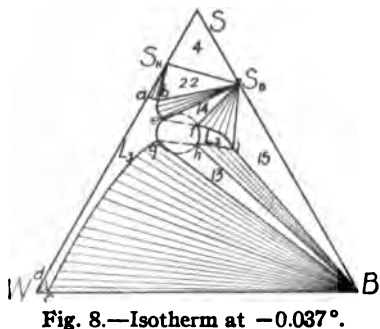
As the temperature is raised above  $-2.7^{\circ}$ , the number of fields in the isotherms increases rapidly, and the changes occur with very small increases in temperature. Fig. 7 represents conditions at a temperature

slightly above this quintuple point. The point *f* of the previous diagram has widened out into the area *f h i* of Fig. 7, indicating the range of composition which the unsaturated solution  $L_2$  may have. By its extension into an area it has given rise to several new equilibria; *e f g h* represents an area of conjugate solutions, for every point in which there should be drawn a tie-line joining the composition of  $L_2$  with that of its conjugate



solution  $L_2$ . The isotherm shows 6 isothermal invariant equilibria indicated by the numbered triangles, 6 isothermal monovariant equilibria consisting of a solid in contact with a liquid and indicated by the shaded areas, an area of conjugate solutions *e f g h*, and 2 areas of unsaturated solutions,  $L_1$  and  $L_2$ , a total of 15 fields.

Increase in temperature produces no change in form until the temperature  $-0.037^\circ$  is reached, at which the change is in one particular only.



The point *c* of the previous isotherm has dropped rapidly until as shown in Fig. 8 it reaches the base line *WB*, thus terminating Equilibrium 18 ( $B + W + L_2$ ) which has existed from  $-57.8^\circ$  up to this temperature. The area *W d c*, representing ice in equilibrium with  $L_2$ , is thus reduced to extremely small dimensions, since the line *W c* represents only the low solubility of benzene in water at this temperature, namely 0.153%

(see Fig. 2). The change occurring as the temperature is raised through the small interval to  $0^{\circ}$  is not represented by a drawing; it consists simply in the fall of the point  $d$  until it reaches the vertex  $W$ . Above this temperature of course the solid phase ice does not appear.

Isotherms will continue to follow the type of Fig. 8, minus the small area  $W d c$ , until Quintuple Point  $C$  is reached at  $+4.98^{\circ}$ . Here the con-

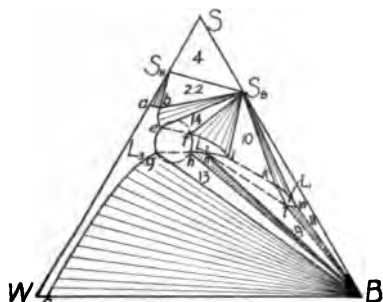


Fig. 10.—Isotherm above  $4.98^{\circ}$ .

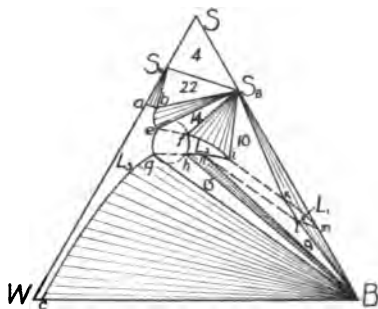


Fig. 11.—Isotherm at  $5.12^{\circ}$ .

ditions will be as shown in Fig. 9, the change being the appearance of the third liquid phase  $L_1$  at the point  $k$ , thus terminating Equilibrium 15 and apportioning its area in the isotherm to the 3 new equilibria, 11, 10 and 9. These represent the new benzene-rich solution in equilibrium with compound and benzene, with compound and  $L_2$ , and with  $L_2$  and benzene respectively.

Fig. 10 represents conditions at a slightly higher temperature, at which

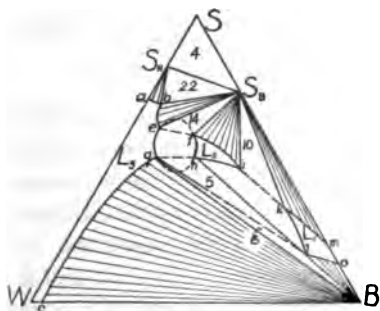


Fig. 12.—Isotherm at  $5.24^{\circ}$  (Quintuple Point B).

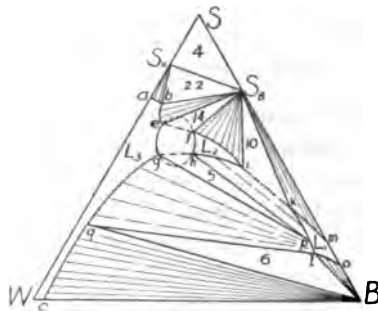


Fig. 13.—Isotherm above  $5.24^{\circ}$ .

$L_1$  has increased its dimensions. Here we have again, as in Fig. 7, the addition of new equilibria involving a solid phase and its saturated solution of varying composition ( $S_B$  m  $K$  and  $B$  m  $l$ ) and also the appearance of  $L_1$  and  $L_2$  as conjugate solutions in the area  $l n i k$ . The total of fields occurring at this temperature is 19, which is the largest number met with in the study of this system. It is worth noting that the solid com-





At a temperature above  $5.24^\circ$ , as shown in Fig. 13, the point *l* will have progressed further downward, and the line *g l* of the preceding isotherm will have broadened into *g p l q*, the area of conjugate solutions of  $L_1$  and  $L_3$ . The length *p l* is exceedingly short in reality, and *g q* quite long, since in all of the distribution curves very small changes in  $L_1$  correspond to very large changes in  $L_3$ . The system is now slightly less complex than in Fig. 10, the number of fields having been reduced to 18, and the simplicity from now on grows rapidly. Fig. 14 shows conditions at a slightly higher temperature, when the point *l* has completed its migration, meeting the line *W B* at the binary quadruple point  $5.40^\circ$  (benzene,  $L_1$ ,  $L_3$ , and vapor). Solid benzene can henceforth exist in equilibrium with only one phase,  $L_1$ , and the area *l o B* is therefore correspondingly small. Equilibrium 6 has been eliminated by the movement of *l*, and the area of conjugate solutions  $L_3-L_1$  (*c g p l*) correspondingly enlarged.

Further rise of temperature of  $0.08^\circ$  results in the movement of the point *o* toward *B*, which it meets at the melting point of pure benzene,

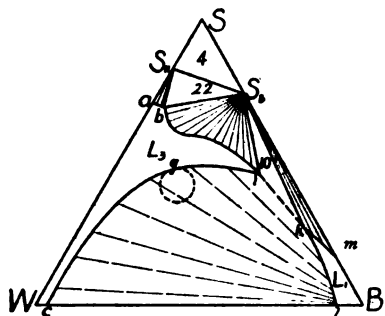


Fig. 16.—Isotherm at  $22.4^\circ$  and above.

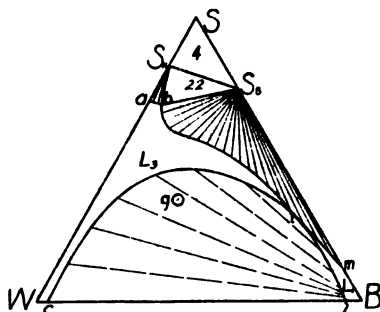


Fig. 17.—Isotherm at  $30^\circ$ .

$5.48^\circ$ , thus removing the area *l o B*, but resulting in no other qualitative change in the isotherm. Above this temperature the chief change is the approach of the points *f* and *e* toward each other, representing the gradual approach of  $L_2$  and  $L_3$  toward identical composition. At  $10.4^\circ$ , the consolute temperature, the isotherm has the form of Fig. 15, and Equilibrium 14 ( $S_B + L_3 + L_2$ ) is terminated.  $L_3$  and  $L_2$ , therefore, have remained as wholly separated areas of unsaturated solution only from  $-2.7^\circ$  to  $+10.4^\circ$ . As the temperature continues to rise, the points *h* and *g*, representing the lower limits of salt concentration in conjugate  $L_3$  and  $L_2$ , also approach each other, merging in the point *g* of Fig. 16 at the sharply defined consolute temperature  $22.4^\circ$ . Equilibrium 5 ( $L_3 + L_2 + L_1$ ) is thereby ended, and it appears, therefore, that three coexistent liquid phases are found in this system only between the temperatures  $5.24^\circ$  and  $22.4^\circ$ . It is noteworthy that this equilibrium does not show the characteristics of the 3-liquid system studied by Schreinemakers,<sup>10</sup> in

which the areas representing the pairs of conjugate solutions migrate toward the 2-component axes, and show after reaching their bases the usual form of 3 binodal curves. In the present system only 1 binodal curve can be shown to reach its 2-component axis, namely the curve  $c g i k l$  (Fig. 16).

If only 1 binodal curve can be completely established, there arises the interesting question as to why there should be found in this system 3 completely separated areas of solution at temperatures below  $10.4^\circ$  (Figures 9 to 15). To account for the separation of the total area of solution into 2 parts ( $L_1$  and  $L_2$ ) is a simple matter; the binodal curve  $c g i k l$  is intersected at  $k$  and  $i$  by the solubility curve  $a b i k m$  at low temperatures, and only when the temperature has risen to  $30^\circ$  (Fig. 17) does the solubility curve rise high enough to escape this intersection. But the further separation of the liquid area into  $L_3$  and  $L_2$  at temperatures below  $10.4^\circ$  (Fig. 15) requires a different explanation. The separation cannot be due to a second intersection of the 2 curves, although the almost perpendicular section of the solubility curve below  $b$  might at first suggest such an intersection. If it is assumed that the solubility curve does have a part descending far enough at any temperature to intersect the binodal curve, it must be granted that it possesses at the same temperature also an ascending branch, since the curve must rise to furnish the upper boundary of the area  $L_2$ . If this loop in the solubility curve exists, its lowermost point must rise with ascending temperature, since the loop is wholly absent at  $25^\circ$  (Fig. 16). In that case, it must on ascending pass through the binodal curve at the point  $g$  (Fig. 16) at a lower temperature than that at which it reaches the point  $e$  (Fig. 15); that is,  $L_3$  and  $L_2$  must become consolute at the concentrations of point  $g$  at a lower temperature than at the point  $e$ . But the experimental facts are in direct opposition to this conclusion; coalescence occurs at  $e$  at  $10.4^\circ$ , and at  $g$  at  $22.4^\circ$ , the difference of  $12^\circ$  being beyond the possibility of experimental error. It follows then that the hypothesis that the separation of  $L_3$  from  $L_2$  is due to a second intersection of the solubility curve and the binodal curve is contradicted by the facts.

The rational explanation seems, therefore, to be that, in Fig. 15, there is a second closed binodal curve  $e g h$ , of which the larger portion is in a stable region and a smaller portion in the metastable region below the binodal curve  $c g i k l$ . At lower temperatures its upper portion is in the metastable region above the solubility curve  $a m$ , as shown by the dotted lines in Figures 7 to 14. The closed binodal curve may be assumed to have its beginning at  $-2.7^\circ$  (Fig. 6) where its stable part is limited to the 2 points  $f$  and  $e$ ; with rising temperature it suffers a contraction in the horizontal dimension and its position in the diagram moves downward, until at  $22.4^\circ$  (Fig. 16) it has moved wholly into the metastable area beneath the bi-

nodal curve  $c k l$ . Since its area becomes rapidly less, it may be assumed to shrink to a point at some temperature not far from  $30^\circ$  (Point  $g$ , Fig. 17), above which temperature it no longer exists.

This hypothesis of a completely closed binodal curve contradicts no facts observed in this study, and is supported by the analytical determination of some of the points which make up its stable part (Equilibrium 14, Fig. 12; Equilibrium 5, Figs. 9 and 11). It is further substantiated by the occurrence of a similar area in the system, a silver perchlorate-toluene, and water, which is now being studied in this laboratory. In this latter case the outlines of the closed curve are very distinctly recognizable. Schreinemakers<sup>13</sup> has postulated the existence of such completely closed binodal curves as the simplest type of binodal curve but, as far as known to me, curves of this character have not previously been realized. In the system under discussion, we may regard the curve as experimentally demonstrated, although certain portions of it are in the metastable region and are therefore not realizable.

The occurrence of this second binodal curve is of course something hardly to be anticipated, since it has been shown that only 1 of the 3 pairs of components in the system shows 2 liquid phases. It is to be recalled however that the curve for the system, silver perchlorate-benzene, (Fig. 1) has very nearly the appearance found where 2 stable liquids occur, and that Alexejew<sup>7</sup> has found the occurrence of 2 liquids in the metastable region for a pair showing a like form of curve. In the case studied by me the 2 liquids have not been found in the metastable region; but it may be held that the addition of the third component, water, has further accentuated the tendency toward the formation of an additional liquid phase, giving rise to a new and stable liquid phase in the 3-component system.

The form of isotherm shown in Fig. 16 is still existent at  $25^\circ$ , at which temperature a complete series of measurements has been made, covering the solubility curve  $a m$ , which is here interrupted over the short distance  $i k$ , and the distribution curve  $c i l$ . The measurements for the solubility curve, which are given in Table IV, were used as a basis for calculating solubilities at all other temperatures.

Within certain limits of compositions of solvent, a single metastable solution is obtained—indeed, cannot apparently be avoided. The experiments numbered 18 to 23 are of this character. At any such total composition, the liquid should break down into  $L_1$  and  $L_2$  in equilibrium with  $AgClO_4 \cdot C_6H_6$  (Equilibrium 10), but actually such solutions remained unchanged for indefinitely long periods. The points 18 to 23 are, however, in no sense indefinite, but fall fairly well upon the smooth curve with no greater error than found in the experiments with the stable solutions.

<sup>13</sup> Schreinemakers, *Z. physik Chem.*, 22, 93 (1897); 23, 649 (1897).

TABLE IV

SOLUBILITY CURVE a m AT 25°					
No.	Point	AgClO <sub>4</sub> %	C <sub>6</sub> H <sub>6</sub> %	H <sub>2</sub> O %	Density
Solid Phase AgClO <sub>4</sub> ·H <sub>2</sub> O					
1	a	84.45	0.0	15.55	2.806
2		84.28	1.19	14.53	2.823
Solid phase AgClO <sub>4</sub> ·H <sub>2</sub> O + AgClO <sub>4</sub> ·C <sub>6</sub> H <sub>6</sub>					
3	b	84.1	1.7	14.2	...
Solid phase AgClO <sub>4</sub> ·C <sub>6</sub> H <sub>6</sub>					
4		83.98	1.68	14.34	2.806
5		83.93	1.36	14.71	2.808
6		83.12	1.55	15.32	2.747
7		81.30	1.41	17.29	2.644
8		75.53	7.75	16.62	...
9		69.27	15.81	14.91	2.103
10		65.69	22.32	11.98	1.978
11		62.34	27.84	9.81	1.871
12		62.01	28.14	9.85	1.851
13		51.89	43.18	4.94	1.562
14		46.80	50.34	2.86	1.462
15		42.51	55.53	1.96	1.358
16		35.20	63.52	1.28	1.254
17	i	(31.92)	(67.03)	(1.04)	(1.200)
18		31.45	67.54	1.01	1.197
19		25.40	73.90	0.70	1.123
20		15.37	84.29	0.34	1.021
21		14.65	85.01	0.34	1.006
22		13.90	85.82	0.28	1.000
23		10.65	89.13	0.22	...
24	k	(10.45)	(89.34)	(0.21)	(0.960)
25		9.55	90.26	0.187	0.949
26		9.38	90.45	0.169	0.9474
27		9.01	90.84	0.15	0.9470
28		8.28	91.60	0.13	0.9367
29		7.31	92.58	0.103	0.9332
30		6.84	93.08	0.074	0.9259
31		6.18	93.77	0.504	0.9221
32		5.96	94.00	0.0361	0.9205
33	m	5.00	95.00	0.000	0.906

The points i and k (Lines 17 and 24), which are the terminations of the areas  $L_3$  and  $L_1$ , could not be found by direct methods, because of the formation of these metastable solutions. The points are placed with reasonable accuracy, however, as the points of intersection of the solubility curve with the distribution curve given later in Table V. The best results were obtained by plotting the concentration of silver perchlorate in terms of normality against the water content on a system of rectangular coördinates; a second plot of the water content against the observed densities gave the density at the point of intersection, supplying all data necessary for the

calculation. Experiment 18 falls upon one of these points of intersection within the probable errors of the determinations.

The curve *a m* as a whole has several points of interest. If the solubility be plotted upon a system of rectangular coordinates, with the concentration of silver perchlorate as ordinate and the percentage composition of the solvent in terms of benzene and water as abscissa, a straight line joining *a* and *m* will then show the solubility at any composition calculated as an additive function of its solubility in the pure solvents. The observed solubilities, however, are found to lie far above the straight line throughout its course, indicating that the mixed solvent is more effective than the pure components in any and all ratios.

The solubility curve in Fig. 16 shows two portions which deviate from the simple curve which might be expected to join the points *a* and *m*. There is a short section which runs nearly parallel to the *W B* axis (Experiments 1, 2, 3, Table IV) followed by a nearly perpendicular portion (Experiments 3 to 8). The curve from Experiments 9 to 30 is practically a smooth curve, giving to the *L<sub>3</sub>* area the general shape of a sickle.

The distribution curve *c i k l* has also been studied at 25°. The method consisted in weighing the components into a small cylinder, rotating at 25° until equilibrium was established, which usually required less than an hour, and then allowing the vessel to stand until the 2 phases were completely clear, which sometimes required a longer period. Samples of each phase were then titrated for their silver content, and a known weight of *L<sub>1</sub>* rotated with a weighed quantity of silver perchlorate and analyzed to determine the benzene-water ratio as explained previously. The volumes of both phases in the original experiment were read in the calibrated cylinder, so that the water and benzene content of the phase *L<sub>3</sub>* was known by subtraction of the composition of *L<sub>1</sub>* from the known total composition. The method of differences thus used leads of course to noticeable irregularity in those experiments in which the benzene concentration of *L<sub>3</sub>* is very low. The following table gives the results found. The figures in brackets were found by graphical interpolation.

The points *i* and *k* (Line 14) were obtained by interpolation, as explained in Table IV, in which also they occur. Experiment 15 represents again a metastable condition; in this case the solutions were supersaturated with respect to the solid phase  $\text{AgClO}_4 \cdot \text{C}_6\text{H}_6$ , since the points fall above the solubility curve. There are, therefore, two kinds of metastability realizable between the points *i* and *k* of Fig. 16, giving, respectively, the metastable liquids described earlier, which should fall at equilibrium into 2 liquid phases each (supersaturation with regard to liquids), and the metastable conjugate solutions of Line 15 (supersaturation with respect to the solid phase). It is interesting to note that the two kinds of metastability have not occurred simultaneously, that is, all points have fallen normally

TABLE V  
THE DISTRIBUTION CURVE c 1 AT 25°  
Conjugate Solutions

No.	$L_2$		$H_2O$ %	Density		$L_1$		$H_2O$ %	Density
	$AgClO_4$ %	$C_6H_6$ %				$AgClO_4$ %	$C_6H_6$ %		
1 c	0.00	0.08	99.92	...	1	0.000	99.95	0.061	...
2	50.81	(0.10)	49.09	1.628		0.080	99.91	(0.06)	0.869
3	59.30	(1.00)	39.70	1.821		0.052	99.89	(0.06)	0.870
4	67.73	1.96	30.31	2.050		0.25	99.69	(0.06)	0.873
5	70.52	3.76	25.72	2.127		0.77	99.17	0.06	0.879
6	69.31	11.17	19.51	2.071		1.55	98.37	0.076	0.881
7	60.06	26.15	13.78	1.749		1.59	98.32	0.090	0.881
8	57.88	30.74	11.38	1.653		1.74	...	...	0.882
9	54.22	36.36	9.42	1.566		1.85	...	...	0.882
10	46.95	47.57	5.47	1.442		2.90	97.00	0.0969	0.891
11	41.74	55.00	3.26	1.348		4.28	95.61	0.119	0.903
12	38.80	58.62	2.57	1.296		5.80	94.05	0.148	0.916
13	35.28	63.23	1.49	1.218		8.42	91.41	0.168	0.937
14 i (31.92)	(67.03)	(1.04)	(1.200)		k (10.45)	(89.34)	(0.21)	(0.960)	
15	31.12	68.06	0.82	1.162		13.58	86.13	0.287	0.983

upon the extension of the solubility curve or of the distribution curve, and not within the area between them.

The distribution curve runs very close to the S W axis up to a concentration of about 65% of silver perchlorate; that is, the amount of benzene in the aqueous layer remains small until the salt concentration becomes very high. It also runs very close to the S B axis up to about 35% of silver perchlorate, showing a correspondingly small amount of water in the benzene layer. The plait point of the curve is in the metastable region between i and k, presumably nearer i than k. As a result of this one-sided location of the plait point, the tie lines for the conjugate solutions are steeply inclined toward the base line W B on the benzene side, which expresses graphically the fact that the distribution of silver perchlorate is largely in favor of the aqueous phase  $L_2$ . Investigation of this distribution at moderate concentrations of salt has already been published:<sup>1</sup> at a salt concentration of 2.4 N in  $L_2$ , the ratio of salt present in  $L_2$  to that in  $L_1$  is at least 46000 to 1, and at lower total salt concentrations the ratio is higher. The bearing of these facts upon the usual views as to the degree of dissociation of the salt in water has been pointed out. When the salt concentration in  $L_2$  has risen as high as 59% (Line 3), the ratio in the 2 phases is still as high as 1200 to 1.

The measurements given earlier in the study of the various equilibria at different temperatures indicate that the distribution curve has substantially the form appearing in Fig. 16, whether the temperature be high or low; that is, it runs close to the S W and S B axes for considerable distances, and reaches its maximum height at a salt concentration between 60% and 70%.

As the temperature rises above  $25^{\circ}$  there is no qualitative change in the isotherm until the temperature is reached at which Equilibrium 10 disappears through the approach of the points *i* and *k* to identical composition, as shown in Fig. 17. This temperature could not be exactly determined, but is not far from  $30^{\circ}$ . The point *i*, which represents the composition of the consolute solutions at that temperature, also represents the plait point of the binodal curve *c l*. Above this temperature we have a continuous area of unsaturated solution extending from the *S W* axis to the *S B* axis, which area grows larger as the temperature rises. At  $42.1^{\circ}$  the last quintuple point appears, as shown in Fig. 18, resulting in the appearance for the first time of the anhydrous compound  $\text{AgClO}_4$ , as the saturating phase in contact with liquid, thereby terminating Equilibria 22 and 4 and originating the new equilibria 1 and 2. Equilibrium 22 has had an existence over a range of  $100^{\circ}$ , and Equilibrium 4, containing no liquid phase, over an indefinitely large temperature range. Of the new equilibria, Equilibrium 1 is but short-lived and disappears

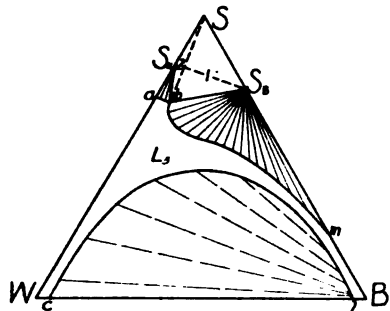


Fig. 18.—Isotherm at  $42.1^{\circ}$  (Quintuple Point A).

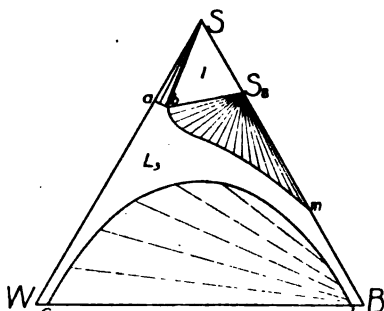


Fig. 19.—Isotherm at  $43.1^{\circ}$ .

at  $43.1^{\circ}$  with the final disappearance of the hydrate as a stable phase; Fig. 19 indicates its disappearance at the point *a*. From this temperature onward the changes consist in a gradual rise of the point *a*, representing the solubility of anhydrous salt in water, and a much more rapid rise of the point *m*, showing the rapid rise in solubility of the compound  $\text{S}_B$ . With these movements there occurs a migration of the point *b* toward the axis *S B*, giving rise (as in Fig. 20) to an increasing area *S a b* in which the anhydrous salt is stable and a diminishing area *S<sub>B</sub> b m* in which the compound  $\text{S}_B$  can exist. The conditions existing at  $100^{\circ}$  are shown qualitatively in Fig. 20.

The continued movement of the point *b* brings it finally to the line *S B* at  $145^{\circ}$ , which is the transition point of the compound into the anhydrous salt. The points *m* and *b*, therefore, meet at this temperature. The isotherm is shown in Fig. 21, which represents the conditions existing at all higher temperatures. All of the monovariant equilibria have dis-



appeared, and no others can be assumed to appear unless the salt forms either a hydrate or a benzene compound with some fractional portion of a molecule of water or benzene; this is rendered improbable by the results shown in Table I and II. It appears, therefore, that above  $145^{\circ}$  the system has but 3 fields, that of the saturated solution,  $S a m$ , that of the conjugate solutions bounded by the binodal curve  $c l$ , and that of unsaturated solution,  $a m l c$ . With rise of temperature the solubility curve  $a m$  rises toward the apex  $S$ , which it should reach at the melting point of the salt,  $480^{\circ}$ . The binodal curve presumably changes its position but slightly. It is of course highly probable that other less simple changes occur before the temperature of  $480^{\circ}$  is reached, since the critical temperatures of both water and benzene are lower than that figure.

We are thus able, from these isotherms, to form an accurate picture of the conditions existing in this 3-component system from the eutectic temperature  $-58.4^{\circ}$ , below which no liquids can exist, up to the melting point of the salt,  $480^{\circ}$ , above which no solid forms can exist.

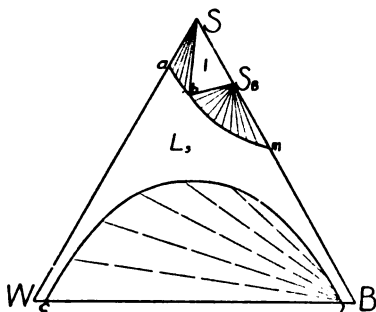


Fig. 20.—Isotherm at  $100^{\circ}$ .

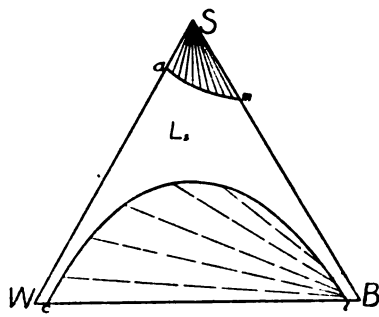


Fig. 21.—Isotherm at  $145^{\circ}$  and above.

### Summary

1. The system, silver perchlorate-water, has a eutectic point at  $-58.2^{\circ}$ , at which temperature the saturated solution contains 73.9% of the silver salt. This is the lowest known eutectic for a true salt and water. The solubility rises to 88.8% at  $99^{\circ}$ .

2. The eutectic temperature of the system, silver perchlorate-benzene, is  $+5.12^{\circ}$ , and the solution contains 3.44% of the silver salt. The solubility curve rises steeply with the temperature, almost reaching a perpendicular form between  $50^{\circ}$  and  $145^{\circ}$ ; at the latter temperature the saturated solution contains 63.0% of silver perchlorate. Attention is called to the likeness between this solubility curve and those which are found where the system gives rise to 2 liquid phases, either in the stable or the metastable region.

3. The hydrate  $\text{AgClO}_4 \cdot \text{H}_2\text{O}$  has been isolated and its transition

point found to be  $43.1^\circ$ ; the compound  $\text{AgClO}_4 \cdot \text{C}_6\text{H}_6$  has also been isolated and its transition point found to be  $145^\circ$ .

4. The ternary system, silver perchlorate-water-benzene is marked by the possession of 6 realizable invariant equilibria, and a large number of monovariant equilibria, affording at least one example of every type of equilibrium theoretically possible for a ternary system containing volatile components.

5. The ternary eutectic representing 3 solid phases, solution and vapor is at  $-58.4^\circ$ ; the eutectic of highest temperature is at  $42.1^\circ$ . The course of the 24 monovariant equilibria originating at these 2 quintuple points and the 4 intermediate quintuple points has been studied.

6. Isothermal diagrams have been constructed to show the various equilibria existing at temperatures between  $-58.4^\circ$  and  $+145^\circ$ .

7. Between  $5.24^\circ$  and  $22.4^\circ$ , 3 coexistent liquid phases can be prepared in stable equilibrium with each other and their vapor. The occurrence of two separate fields of unsaturated solution is explained as due to the intersection of the solubility curve of silver perchlorate with the binodal curve representing the limited solubility of benzene and water. The occurrence of a third field is explained as due to the existence, between  $-2.7^\circ$  and  $+30^\circ$  (approximately), of an additional closed binodal curve, which does not extend to any one of the 2-component axes at any temperature. It appears to be the first demonstrated case of a closed binodal curve.

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[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY, UNIVERSITY OF MINNESOTA]

## A SIMPLE METHOD OF ELECTROMETRIC TITRATION IN ACIDIMETRY AND ALKALIMETRY

BY PAUL FRANCIS SHARP WITH F. H. MACDOUGALL

Received November 29, 1921

The object of the investigation reported in this paper was to find a number of constant and reproducible electrodes which would be electromotively equivalent to hydrogen electrodes dipping in solutions of various known concentrations of hydrogen ion. The usefulness of such electrodes will be at once apparent. If, for example, it becomes necessary to titrate an unknown acid solution to an end-point which shall be a definite hydrogen-ion concentration, the half-cell containing a hydrogen electrode and the unknown solution is connected with one of our electrodes and alkali is run into the unknown solution until a galvanometer indicates a zero e.m.f. The method is applicable especially to all cases in which the titration is carried to a definite hydrogen-ion concentration, or more generally to all cases in which the correct potential difference at the electrode in the solution at the end of the titration is known in advance.

After we had practically completed our investigation, we found that Pinkhof<sup>1</sup> had constructed various cadmium electrodes with the same purpose in mind. His electrodes cover the range of hydrogen-ion concentrations from  $10^{-6}$  to  $10^{-10}$ . His results are reproduced in Table I. He used electrodes which were 11–13% cadmium amalgam.

TABLE I  
EXPERIMENTS OF PINKHOF

Composition of electrode solution		Potential against 0.1 N KCl calomel electrode	Equivalent to a hydrogen electrode in a solution of hydrogen-ion concentration
Salt	N		
Cd(NO <sub>3</sub> ) <sub>2</sub> .....	1.3	0.696	$10^{-6}$
CdCl <sub>2</sub> .....	0.1	0.754	$10^{-7}$
CdI <sub>2</sub> .....	0.1	0.812	$10^{-8}$
KI.....	0.21		
CdI <sub>2</sub> .....	0.01	0.870	$10^{-9}$
KI.....	0.6		
CdI <sub>2</sub> .....	0.01	0.929	$10^{-10}$
KI.....	1.05		

After investigating a large number of electrodes, we also found that the cadmium electrodes were the ones best adapted for the range  $10^{-6}$  to  $10^{-10}$ . As our measurements were made with apparently greater accuracy, and as, in addition, we found suitable lead electrodes for the range of  $10^{-4}$  to  $10^{-6}$ , we feel that it would be desirable to make our results available.

The reference electrode used in standardizing our half-cells was the *N* potassium chloride calomel electrode recommended by Lewis, Brighton, and Sebastian,<sup>2</sup> who give 0.2828 volt at 25° as the e.m.f. of the combination: H<sub>2</sub>(1 atm.), H<sup>+</sup>(*M*) || KCl(0.1 *M*), KCl(*M*), HgCl, Hg.

The results given in Table II are the average of all of a number of determinations, the comparisons being made against at least 4 different calomel cells. None of the determinations differed from the averages given in the table by more than 0.0002 volt. All measurements were made with cells immersed in a water-bath kept at a temperature of 25° ± 0.01°.

The mercury used in this work was purified by spraying it several times into dil. nitric acid and then distilling it under reduced pressure. The amalgams were 12 to 12.5% of lead or cadmium. They were prepared by heating the weighed materials until solution was complete and then filtering the liquid while hot through a filter paper with a pinhole in it. The calomel for the reference electrodes was prepared by electrolysis of approximately 2 *N* hydrochloric acid, using a rotating mercury anode and a small platinum wire cathode.<sup>3</sup>

<sup>1</sup> Pinkhof, *Chem. Weekblad*, 16, 1168 (1919).

<sup>2</sup> Lewis, Brighton, and Sebastian, *THIS JOURNAL*, 39, 2245 (1917).

<sup>3</sup> Lipscomb and Hulett, *ibid.*, 38, 20 (1916). Hulett, *Phys. Rev.*, 22, 47 (1906). Wolff and Waters, *Bur. Standards Reprint* No. 70 (1907).

Calomel prepared by this method was compared with calomel obtained by precipitation, but no differences greater than 0.0002 volt were detected in cells using the two kinds of calomel.

The potassium chloride was of C.P. grade and was recrystallized several times, although no difference was detected between the cells made with the recrystallized material and those made with the C.P. salt. Lead iodide was prepared from C.P. lead acetate and potassium iodide and washed by decantation. Two different samples of cadmium sulfate and 3 different samples of potassium iodide, all of C.P. grade, were compared and found to give identical results within the limits of the experimental errors.

All salts used were dried at 500° for several hours and preserved in tightly stoppered bottles.

To simplify the preparation of the electrode solutions, Col. 1 of Table II gives the number of cubic centimeters of stock solutions of 0.5 *N* cadmium sulfate and 2.0 *N* potassium iodide which on dilution to a total volume of 100 cc. will give an electrode solution of the proper concentration.

As several of the common proteins have their iso-electric point near a hydrogen-ion concentration of  $10^{-4.7}$ , an electrode was constructed corresponding to this concentration.

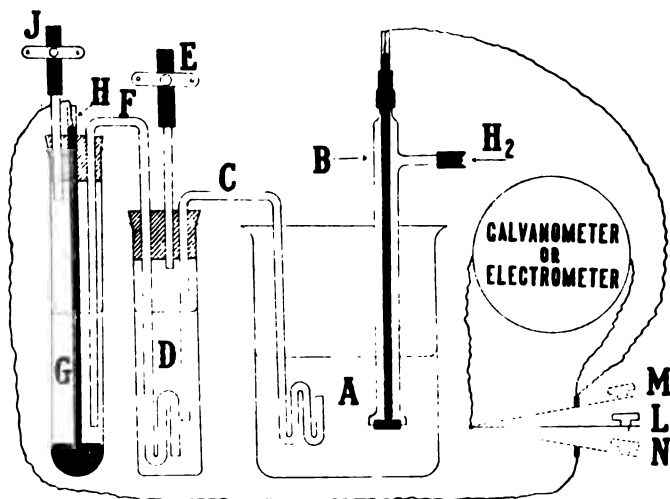
TABLE II  
EXPERIMENTAL DATA

Electrode solution Dilute quantities given to total volume of 100 cc.			Potential against normal calomel electrode	Calculated potential of hydrogen electrode in solutions of indicated hydrogen-ion concentration	
12-12.5% Lead amalgam and lead iodide					
Cc.	N	Salt			
0.52	2	KI	0.5195	0.5194	10 <sup>-4</sup>
2.90	2	KI	0.5609	0.5608	10 <sup>-4.7</sup>
6.14	2	KI	0.5786	0.5786	10 <sup>-5</sup>
67.50	2	KI	0.6378	0.6377	10 <sup>-6</sup>
12-12.5% Cadmium amalgam					
100.00	0.5	CdSO <sub>4</sub>	0.6967	0.6968	10 <sup>-7</sup>
0.20	2.0	KI			
10.00	0.5	CdSO <sub>4</sub>	0.7560	0.7560	10 <sup>-8</sup>
10.14	2.0	KI			
100.00	0.5	CdSO <sub>4</sub>	0.8150	0.8151	10 <sup>-9</sup>
26.40	2.0	KI			
2.00	0.5	CdSO <sub>4</sub>	0.8742	0.8743	10 <sup>-10</sup>
48.70	2.0	KI			

### Experimental Arrangements

The apparatus and method of use are indicated in Fig. 1. It may be sufficient to state that B is a dipping hydrogen electrode of the Hildebrand<sup>4</sup> type. Siphon C and Vessel D contain saturated potassium chloride. The liquid to be titrated is placed in the beaker A. Siphon F and vessel G contain the electrode solution. Through mercury in the glass

<sup>4</sup> Hildebrand, THIS JOURNAL, 35, 847 (1913).



tube H, connection is made by means of a platinum wire with the lead or cadmium amalgam at the bottom of the electrode vessel G.

### Summary

Employing electrodes of lead amalgam and of cadmium amalgam, the authors have prepared a series of half-cells which are electromotively equivalent to hydrogen electrodes in contact with solutions in which the hydrogen-ion concentrations are, respectively,  $10^{-4}$ ,  $10^{-4.7}$ ,  $10^{-5}$ ,  $10^{-6}$ ,  $10^{-7}$ ,  $10^{-8}$ ,  $10^{-9}$ ,  $10^{-10}$ .

MINNEAPOLIS, MINNESOTA

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE OHIO STATE UNIVERSITY]

## MEASUREMENT OF SOLUBILITY BY FLOATING EQUILIBRIUM. THE SOLUBILITY OF LEAD ACETATE

BY MERLE L. DUNDON AND W. E. HENDERSON

Received December 5, 1921

### Introduction

It has been shown by Richards and Shipley<sup>1</sup> that a small glass float of suitable size and shape, completely immersed in a liquid, is sensitive to very small changes in the density of that liquid. They have applied this principle to the quantitative analysis of solutions and to the calibration of thermometers.

Lamb and Lee<sup>2</sup> have by a slightly different procedure measured the density of various solutions with an accuracy of one part in the seventh

<sup>1</sup> Richards and Shipley, *THIS JOURNAL*, **34**, 599 (1912); **36**, 1 (1914).

<sup>2</sup> Lamb and Lee, *ibid.*, **35**, 1666 (1913).

decimal place. Their float consisted of an inverted 250cc. flask with an iron rod sealed within it. The densities were determined by weights added to the sinker together with measurement of the current in an electromagnet placed below the float and necessary to cause the latter to sink.

For some time in this laboratory the same general principle has been applied to the measurement of the solubility of a salt at various temperatures. The method that has been developed consists in adding a known weight of solvent to a saturated solution of unknown concentration, until the solution attains the same density as a glass float calibrated at a definite arbitrary temperature. The density of the float used is made less than the density of the most dilute solution to be analyzed, so that it will always be necessary to add solvent to any unknown sample to bring it to the density of the float. It is evident that for a given float and at a fixed temperature, the percentage of solid in the equilibrium solution of any given solute is constant. Therefore, the weight of solute in a given sample of unknown concentration is obtained by first bringing the solution to the same density as the float and then multiplying the weight of the resulting equilibrium solution by that fraction which it is known from the calibration of the float to contain. From the weight of salt obtained in this way and the weight of sample taken the solubility can be calculated with ease.

**Purpose of This Investigation.**—The purposes of the work herein described were (1) to study the method of determining solubilities by floating equilibrium, and (2) to determine accurately the solubility of lead acetate,  $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 3\text{H}_2\text{O}$ , over a definite range of temperature.

### Experimental

**Preparation of the Pure Salt.**—A commercial c. p. lead acetate was recrystallized twice from distilled water made distinctly acid with acetic acid. Residues obtained during the investigation were recrystallized in the same way and used again. Qualitative tests for impurities gave negative results when applied to the prepared salt. The crystals were usually filtered from the mother liquor on a Büchner funnel, washed once with boiled, distilled water and kept in a glass-stoppered bottle from which separate portions were used from day to day. In order to determine whether the crystals obtained were really the hydrated normal acetate,  $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 3\text{H}_2\text{O}$ , a sample was very carefully dried and analyzed as follows. A current of washed air was drawn through a tube of partially dehydrated crystals and then through the sample to be dried. In this way the loss of any water of hydration and the formation of any basic salt were prevented. The dried sample was weighed in a platinum crucible, dil. sulfuric acid added and the crucible placed in an oven at  $110^\circ$  until the water and acetic acid were removed. The resulting lead sulfate was freed from sulfuric acid by heating to a bright red heat in an electric furnace. From the weight of lead sulfate the equivalent weight of lead acetate was calculated, all weights being reduced to the vacuum basis. The results of three analyses are as follows: weights taken, 1.0827, 1.2933 and 1.1673 g.; weights calculated from analysis, 1.0827, 1.2936 and 1.1674 g.

**Calibration of the Float.**—A cigar-shaped float was made from a piece of ordinary soft glass tubing and approximately the desired density ob-

tained by sealing within it a small globule of mercury. The density was made slightly less than that of the saturated solution of lead acetate at 0°. This float was then carefully calibrated as follows. Two separate samples of solution of about 250 cc. each were very carefully brought to floating equilibrium at 25°. Two samples of each were pipetted into a platinum crucible in a glass-stoppered weighing bottle and weighed. Sulfuric acid was then added, the solution evaporated in an oven and the lead sulfate ignited to a bright red heat in an electric furnace. The results are given below with weights reduced to a vacuum. The last two columns are expressed in terms of anhydrous salt.

Sample	Wt. of soln. G.	PbSO <sub>4</sub> G.	PbAc <sub>2</sub> calculated G.	PbAc <sub>2</sub> in solution %
1	19.5958	3.0020	3.2198	16.431
2	16.3442	2.5025	2.6841	16.422
3	18.2169	2.7891	2.9915	16.421
4	18.3582	2.8110	3.0151	16.423

The average of the last three values, which check very closely, is 16.422% and was the value selected to represent the floating equilibrium solution.

**Apparatus and General Method.**—A large thermostat which could be regulated to 0.01° was kept at 25° and was used in bringing the solution of unknown concentration to floating equilibrium. The thermometer used was graduated in tenths of a degree and had been checked by the Bureau of Standards.

Saturations were attained in a 10-liter thermostat which could be regulated to about 0.02°. The following general procedure was used. An excess of crystals roughly weighed was put into a flask with boiled, distilled water and the solution was stirred with a small propeller-shaped, motor-driven stirrer. The temperature was kept for a few minutes from 0.5° to 3.° higher than that desired and then stirring continued at a constant temperature for about 20 hours. At least two samples were taken for float tests at intervals from 1 to 3 hours apart and one for a gravimetric test within that time. Gravimetric tests were made in the same way as in the calibration of the float.

In making a determination by the float method a 100cc. glass-stoppered weighing bottle was used, and a stirrer was made for it by bending a loop on the end of a small glass rod. The float and stirrer were placed in the weighing bottle and the whole apparatus weighed. The solution for analysis was pipetted into the bottle with a warm pipet and the weight again taken. In case the temperature of the unknown solution differed much from that of the room, this sample was placed in a desiccator for some time before weighing. The stopper was removed, water was added rapidly until the solution began to approach the density of the float,

and the open bottle was then placed in a thermostat regulated at 25°. After sufficient time for the temperature to become constant, water was added a drop at a time from a capillary pipet with constant stirring until floating equilibrium was reached. The end-point was considered to be that point at which the float would just sink when suspended in the solution. It could be determined within one small drop of water. If the end-point was passed, solvent was removed by blowing a current of dry air over the surface for a few minutes. The bottle containing the equilibrium solution was then stoppered, wiped carefully with a piece of clean cheese cloth, and weighed. Before weighing it was placed in a desiccator for about 10 minutes. In a typical analysis of a solution saturated at 20° the vacuum weight of the solution taken was 41.0925 g., and that of the equilibrium solution was 76.7818 g. The salt content of the equilibrium solution as shown by the calibration of the float was 16.422%.

$76.7818 \times 0.16422 = 12.6091$  g. of  $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$  in 41.0925 g. of solution.

$$\frac{12.6091}{41.0925} = 30.684 \% \text{ Pb } (\text{C}_2\text{H}_3\text{O}_2)_2 \text{ in the solution.}$$

$$\frac{12.6091 \times 100}{41.0925 - 12.6091} = 44.268 \text{ g. of Pb}(\text{C}_2\text{H}_3\text{O}_2)_2 \text{ in 100 g. of water.}$$

The data obtained on the solubility of  $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 3\text{H}_2\text{O}$  and the densities of the saturated solutions are given in Table I. All weighings were reduced to a vacuum basis by the method given in Circular 19 of the Bureau of Standards. Densities obtained from standard tables were used as follows:  $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 3\text{H}_2\text{O}$ , 2.5;  $\text{PbSO}_4$ , 6.23. Densities of solutions were determined by weighing the volume contained in a 1cc. pipet. For the equilibrium solution the value was 1.13.

TABLE I  
SOLUBILITY OF  $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 3\text{H}_2\text{O}$  PER 100 GRAMS OF WATER  
Expressed in terms of anhydrous salt

Temperature	Float method	Gravimetric method	Density of solution saturated
°C.	G.	G.	
0.10	19.84	19.82	1.14
0.20	19.93	....	..
10.00	29.46	29.37	1.195
...	29.38	....	..
15.00	35.84	35.82	1.22(interp.)
...	35.81	....	..
20.00	44.27	44.25	1.26
...	44.24	....	..
25.00 <sup>a</sup>	55.195	55.21	1.33
30.02	69.95	69.95	1.41
...	69.92	....	..
35.04	88.96	89.01	1.48



TABLE I (continued)

Temperature °C.	Float method G.	Gravimetric method G.	Density of saturated solution
...	89.05	....	..
40.07	116.69	116.55	1.60
...	116.73	....	..
45.10	155.71	155.49	1.73
	155.66		
	155.66		
50.14	221.44	220.27	1.88
	221.14		
50.14 <sup>a</sup> (Next day)	222.42		

<sup>a</sup> See discussion under behavior of lead acetate in neutral solution.

TABLE II

THE SOLUBILITY OF  $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 3\text{H}_2\text{O}$  AS TAKEN FROM A CURVE PLOTTED FROM THE VALUES IN TABLE I AND EXPRESSED IN TERMS OF THE ANHYDROUS SALT

Temperature °C.	Grams per 100 g. of water	Per cent. solution
0	19.7	16.5
5	23.7	19.4
10	29.3	22.8
15	35.6	26.4
20	44.3	30.7
25	55.2	35.6
30	69.7	41.1
35	88.9	47.1
40	116.0	53.7
45	153.0	60.7
50	221.0	67.6

**Conclusions in Regard to the Float Method.**—From the results obtained we can safely say that analyses by the float method can easily be made to check within 0.1% without taking extraordinary precautions. With as soluble a salt as lead acetate the change of solubility with temperature is so great that slight variations in the temperature of saturation have a large effect upon the concentration of the solution. For example, at 35° a change of 0.02° corresponds to a change of solubility of about 0.1%. Thus it seems probable that in this work the method of analysis was much more accurate than the attainment of solubility equilibria. The attainment of floating equilibrium is a process capable of great exactness, and if we assume that density under standard conditions is a true measure of concentration, as it undoubtedly is in most cases, then the accuracy of this method of analysis is determined largely by two factors, thermostat regulation and weighing in a large glass vessel. If, however, the weighings are done with great care such errors will be less than the weight of the last drop used in bringing the solution to equilibrium. The

average weight per drop as we worked was 0.035 g. (added to about 40 g. of solution). For the best results the density of the float should be such that the weight of solution taken for analysis is about the same as the weight of solvent to be added. This will minimize errors in weighing. The larger the volume of the equilibrium solution the more accurately the end-point can be reached; but a very large volume is more difficult to weigh with precision. From 50 to 75 g. of equilibrium solution is a very satisfactory quantity. Care must be taken that bubbles of air do not cling to the float, and in determining an equilibrium the float must be pushed into the center of the solution as it clings to the upper surface with great tenacity.

The time necessary for a complete analysis is determined largely by the time required for weighing. With some practice the float can easily be brought to equilibrium within 15 minutes. Altogether the method is capable of considerable speed and accuracy.

In working with a substance which can readily be obtained in a pure form the float may be calibrated most easily by weighing directly the pure substance and the resulting equilibrium solution which is obtained by adding the solvent.

**The Behavior of Lead Acetate in Solution.**—The value for the solubility of normal lead acetate which seems to us most accurate is that given by Jackson.<sup>3</sup> He worked only at 25°, and in a study of the basic acetates of lead by interpolating the curve across the neutral point, obtained the value for the normal salt. His value is 35.5%, or 55.05 g. per 100 g. of water. The only other value of any importance which we have found is that of Osaka and Hara<sup>4</sup> who determined the solubility in dil. acid solutions and extrapolated to neutral solution. Their value at 25° is 54.38 g. per 100 g. of water.

From 12 gravimetric analyses on 4 different solutions we obtained the average value 55.21. After the values at other temperatures had been obtained we returned to 25°, and on a solution of carefully prepared crystals, two float tests checked at 55.46 which is considerably higher than before. Some well formed crystals were then very carefully washed and immediately placed in the saturation flask. By the float method 55.50 and 55.53 g. per 100 g. of water were obtained; by the gravimetric method, 55.46 g.

It seemed as a result of these experiments that the more carefully we prepared the salt the higher were the values and the more deviation they showed from the results obtained indirectly by Jackson. Moreover, another very interesting fact came to light in the temperature curve. Below 35° the float values and the gravimetric values checked very well,

<sup>3</sup> Jackson, *THIS JOURNAL*, 36, 2350 (1914).

<sup>4</sup> Osaka and Hara, *Mem. Coll. Sci. Kyoto Imp. Univ.*, 2, 147 (1917).

but at higher temperatures the gravimetric curve began to fall definitely below the curve obtained by the float method. These facts seemed to require some explanation.

Jackson<sup>3</sup> has shown that upon the addition of lead hydroxide to solutions of normal acetate a very soluble salt of the composition  $3\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot \text{PbO} \cdot 3\text{H}_2\text{O}$  is formed. Parsons<sup>4</sup> has also shown that the freezing point of a solution of normal lead acetate is actually raised by the addition of lead hydroxide, which confirms this fact. By these two salts dissolving independently it is evident that the presence of a slight amount of basic lead would increase very greatly the apparent solubility of the normal salt. At high temperatures the hydrated salt decomposes with the evolution of water and acetic acid so readily that it is impossible to determine its melting point in an open tube. Löfman<sup>5</sup> has shown that at  $20^\circ$  hydrolysis is considerably more than 1%. This hydrolysis would produce a basic salt and free acetic acid. As the acid concentration increased the hydrolysis would be retarded, unless the temperatures were high enough to drive off the acid, in which case the action would proceed indefinitely. Because of the very small ionization of lead acetate a very low acid concentration should effectually retard hydrolysis. A mass of fine crystals taken from an acid solution might carry with them a slight amount of acid which would affect the apparent solubility. This could account for the variable results at  $25^\circ$ . At higher temperatures the formation of basic salt would be greater, and a calculation of normal salt based on total lead content would necessarily be different from a calculation based on the density of the solution. This result is in accordance with the facts. It is probable, therefore, that the values obtained by both methods are influenced to some extent by this effect.

Jackson gives the following figures for slightly acid and slightly basic solutions at  $25^\circ$ .

	PbO %	$\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$ %	Density of sol.
1	-0.27	35.19	1.326
2	+0.10	35.60	1.334
3	+1.01	37.14	1.367

Calculating total lead as  $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$  these would be (1) 54.30, (2) 55.43, and (3) 60.57 g. per 100 g. of water. The density of one of our solutions which analyzed 55.23 was 1.333 which agrees quite well.

The assumption made above that the variable results are due to the presence of basic salt seems to be justified by all available experimental data. If, therefore, solubility is the amount of salt that goes into solution with water, our values are reasonably accurate. If it is a measure of

<sup>3</sup> Parsons, *J. Phys. Chem.*, 11, 659 (1907).

<sup>5</sup> Löfman, *Z. anorg. allgem. Chem.*, 107, 241 (1919).

the number of molecules of normal salt in the solution, our values are probably a little high. For all practical purposes, however, the difference is not appreciable.

For assistance rendered in the earlier stages of this work, credit should be given to Mr. Gebhard Stegeman.

### Summary

A method of determining solubilities by the use of floating equilibrium is described. This method has been shown to be capable of considerable speed or great accuracy and a reasonable amount of both.

The solubility of lead acetate,  $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 3\text{H}_2\text{O}$ , has been determined between  $0.0^\circ$  and  $50^\circ$ .

Evidence has been produced which supports an explanation for the variation in the values obtained for the solubility of lead acetate.

COLUMBUS, OHIO

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[CONTRIBUTION FROM THE MUSPRATT LABORATORY OF PHYSICAL AND ELECTRO-CHEMISTRY, UNIVERSITY OF LIVERPOOL.]

## THE INFLUENCE OF ELECTROLYTES ON THE SOLUBILITY OF NON-ELECTROLYTES

By ANDREW McKEOWN

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The mutual relations existing between the solubilities of different substances in the same solution have received much attention in the past, both from the theoretical and from the practical standpoint, and semi-empirical relations have been obtained which represent the experimental facts in particular cases in a more or less satisfactory manner.<sup>1</sup> Investigations have recently been carried out by Dawson<sup>2</sup> on the salting out of phenol from water solution by sodium sulfate, and by Thorne<sup>3</sup> on the solubility of ethyl ether in aqueous solutions of sodium chloride. The data in the latter case are of special interest, since the solubility determinations have been carried out at two different temperatures, *viz.*,  $15^\circ$  and  $25^\circ$ . Thorne finds that his results conform to the equation

$$\frac{1}{c} : \log_{10} \frac{s_0}{s} = k$$

where  $c$  is the concentration of sodium chloride present in solution,  $s$  is the corresponding solubility of ethyl ether,  $s_0$  is the solubility of ether in pure water, and  $k$  is a constant for a given temperature, having the value 0.0555 at  $15^\circ$  and 0.0536 at  $25^\circ$ . As a matter of fact, the solubility of ether in pure water is anomalous, but the equation holds fairly

<sup>1</sup> Compare Rothmund, *Z. Elektrochem.*, **14**, 532 (1908); *Z. physik. Chem.*, **69**, 523 (1909).

<sup>2</sup> Dawson, *J. Soc. Chem. Ind.*, **39**, 151T (1920).

<sup>3</sup> Thorne, *J. Chem. Soc.*, **119**, 262 (1921).

accurately for the solubilities of ether,  $s_1$  and  $s_2$ , in salt solutions of concentrations  $c_1$  and  $c_2$ .

From Thorne's data the heats of solution of ether in the various sodium chloride solutions can be calculated by means of the equation

$$\frac{d(\ln s)}{dT} = \frac{\text{heat absorbed}}{RT^2} \quad (1)$$

The use of this expression involves the assumption that solubility  $s$  is closely analogous to a true equilibrium constant. This assumption will be considered later.

If the heat absorbed remains constant over the temperature range  $15^\circ$  to  $25^\circ$ , the above equation may be integrated between these limits giving

$$\ln \frac{s'}{s} = \frac{Q}{R} \left( \frac{1}{T'} - \frac{1}{T} \right) \quad (2)$$

where  $Q$  is the heat evolved per mole of ether dissolved. From the equation,  $Q$  may be calculated in the different cases treated by Thorne.

TABLE I  
CALCULATION OF HEAT OF SOLUTION OF ETHER IN SODIUM CHLORIDE SOLUTION

NaCl per 100 g. of soln. G.	Solubility, $s'$ , of ether at $15^\circ$	Solubility, $s''$ , of ether at $25^\circ$	$Q$ Cal.
0	8.43	6.05	5635
1	8.06	5.98	5073
2	7.09	5.28	5010
4	5.49	4.13	4838
5	4.84	3.65	4794
6	4.26	3.22	4754
8	3.30	2.52	4584
10	2.55	1.97	4383
15	1.35	1.11	3327
20	0.71	0.57	3734 (?)
25	0.37	0.31	3007

It will be observed that the heat evolved decreases steadily with increasing salt concentration. It is suggested that this decrease may be related to the decrease in the solubility of the ether in the following manner.

If we assume solubility to be analogous to a true equilibrium constant (as the above use of the van't Hoff isochore relation implies) we may write the solubility  $s$  in moles per liter as equal to: velocity constant of "dissolution"/velocity constant of "precipitation." Let us consider the mechanisms of the dissolution and precipitation processes. The former consists essentially of an ejection of solute molecules from the solid or liquid phase of undissolved solute into the adjoining layer of solution. The expression for the rate of dissolution is, therefore, of the same form as that applying, for example, to the rate of vaporization of molecules from the surface of a liquid, or the rate of thermionic emission of electrons from a

metal surface. The rate of the latter is given by Langmuir<sup>4</sup> from kinetic theory considerations as

$$n = N \sqrt{\frac{kT}{2\pi m}} e^{-w/kT}$$

where  $n$  is the number of electrons escaping from unit surface per second,  $N$  is the number of electrons of mass  $m$  per unit volume of the emitting substance, and  $w$  is the work required to carry an electron through the surface of the metal. We may by analogy write the rate of dissolution, or the number of molecules dissolving per square centimeter per second

$$n_0 = N_0 \sqrt{\frac{RT}{2\pi M}} e^{-E_0/RT} \quad (3)$$

where  $N_0$  is the number of molecules per cc. of undissolved solid or liquid,  $M$  is the molecular weight of the solute, and  $E_0$  is the work required in the dissolution of one mole of solute, that is, the critical increment of dissolution.

In the precipitation process, we have to consider the number of solute molecules in solution which collide on one square centimeter of the surface of the solute phase per second, together with the fraction of these which condense on collision. The first is given by  $kN \sqrt{\frac{RT}{2\pi M}}$ , and the number condensing by

$$n = k N \sqrt{\frac{RT}{2\pi M}} e^{-E/RT} \quad (4)$$

where  $E$  is the critical increment of condensation, and  $k$  is a factor introduced to take account of the specific rate of diffusion of the solute molecules up to the bounding surface. For the moment we will regard  $k$  as a constant at constant temperature, independent of the concentration of the salt solution. When solution has reached its limit, the rates (3) and (4) are equal, so that

$$N = \frac{N_0}{k} \cdot e^{-(E_0 - E)/RT} \quad (5)$$

where  $N$  is the number of solute molecules per cc. of solution, and is a measure of the solubility.

Now the heat evolved is the difference of the critical increments of resultants and reactants, that is  $E - E_0 = \text{heat evolved} = Q$ . Hence

$$s = A \cdot e^{Q/RT} \quad (6)$$

where  $A$  is provisionally a constant determined by  $k$  and  $N$ .

If we denote by  $s_1$  the solubility of ether in a 1% solution of sodium chloride at a temperature  $T$ , and by  $s_n$  the solubility in any given salt solution at the same temperature, we have

<sup>4</sup> Langmuir, *J. Am. Electrochem. Soc.*, 29, 12 (1916).

$$\log s_1 = \log A + \frac{Q_1}{RT}$$

$$\log s_n = \log A + \frac{Q_n}{RT}$$

Hence

$$RT \log \frac{s_1}{s_n} = Q_1 - Q_n \quad (7)$$

In the following table the values of  $RT \log s_1/s_n$  at the temperatures 15° and 25° (Cols. 2 and 3) are compared with the values  $Q_1 - Q_n$  obtained by use of the van't Hoff isochore (compare Table I). In order to reduce the solubility data given by Thorne in grams per 100 g. of solution to grams per 100 cc. of solution, that is, in order to express  $s_1$  and  $s_n$  in volume concentration terms, it is necessary to multiply the ratio of Thorne's values by  $d_1/d_n$ , the ratio of the densities of the solutions.

TABLE II

NaCl conc. limits per 100 g. of soln. G.	$RT \log \frac{s_1}{s_n}$ at 15°	$RT \log \frac{s_1}{s_n}$ at 25°	$Q_1 - Q_n$ from Table I
1-2	69.2	69.4	63
1-4	207	206	235
1-5	275	275	279
1-6	346	334	319
1-8	482	481	490
1-10	621	618	690
1-15	964	936.5	1746 (?)
1-20	1310	1309	1339
1-25	1662	1647	2066

The values corresponding to  $s_0$  have been omitted from the above table, since they are at very great variance with one another. Thus 26, 7, 570 are the figures for Cols. 2, 3 and 4, respectively. It is difficult to explain why so great a discrepancy is shown when the solubilities of ether in pure water are employed. Thorne himself has already commented on the abnormality of these data.

The values of  $Q_1 - Q_n$  in Col. 4, obtained from the van't Hoff isochore, agree on the whole (with one exception) with the figures in the two preceding columns. It is easily seen that this result justifies the assumption used above that the factor  $k$  is independent of the concentration of the salt solution. Again, if the values in Cols. 2 and 3 were identical, Col. 4 should correspond strictly to either, since the van't Hoff isochore can be deduced from the statistical equation (7) at two different temperatures thus

$$RT' \log \frac{s_1'}{s_n'} = Q_1 - Q_n$$

$$RT'' \log \frac{s_1''}{s_n''} = Q_1 - Q_n$$

therefore

$$\log \frac{s_1'}{s_n'} - \log \frac{s_1''}{s_n''} = \frac{Q_1 - Q_n}{R} \left( \frac{1}{T'} - \frac{1}{T''} \right)$$

which is the equation from which the values of  $Q_1 - Q_n$  of Col. 4 are calculated (the ratio of the densities of the two solutions at the two different temperatures being taken as equal). The large divergence to be observed in a few cases (especially for the 1-15% sodium chloride solutions) is considered to be due entirely to multiplication of the error initially present in the solubility data. Indeed, an examination of these data shows that the ether solubilities given by Thorne do not decrease in a perfectly regular manner as the sodium chloride concentration increases. This is especially true for the data referring to 25°. We are, therefore, justified in taking Col. 2, in preference to Col. 3 or 4, as the most accurate measure of the differences of the heats of solution of ether in various sodium chloride solutions.

Finally, the fact that from Equation 7, based on statistical principles, we may deduce an equation of the form

$$\log \frac{s_1'}{s_1} - \log \frac{s_n'}{s_n} = \frac{Q_1 - Q_n}{R} \left( \frac{1}{T'} - \frac{1}{T''} \right)$$

which is the difference of two van't Hoff isochores, is evidence in favor of the general correctness of our original mechanism of solubility from which Equation 7 is derived.

The effect of an electrolyte on the solubility of a non-electrolyte may be looked at from a slightly different point of view. Nernst and Jahn have treated in a semi-empirical manner the corrections to be applied to the thermodynamic properties of each constituent of a solution due to the mutual influences of the components, and the latter writer<sup>5</sup> has applied his concepts with considerable success to explain the anomaly of strong electrolytes and the departure of the electromotive force of concentration cells from the values calculated from the simple Nernst formula.

Rothmund, by a similar line of treatment<sup>6</sup> deduces the following relation between the solubilities ( $\eta_4$  and  $\eta'_4$ ) of a non-electrolyte in water and in a salt solution of concentration  $c$

$$RT \log \frac{\eta_4}{\eta'_4} = \alpha_{1,4} c_1 + 2\alpha_{2,4} c_2 \quad (8)$$

where  $c_1$  is the concentration of the undissociated salt, and  $c_2$  is the concentration of either ion;  $\alpha_{1,4}$  and  $\alpha_{2,4}$  are factors representing the respective specific influences of the undissociated molecule and either ion on the properties of the non-electrolyte.

Since it is reasonable to assume that the specific mutual influence of two molecules is small compared with that of an ion and a molecule,  $\alpha_{1,4}$  is put equal to zero, giving

$$RT \log \frac{\eta_4}{\eta'_4} = 2\alpha_{2,4} c_2 \quad (9)$$

<sup>5</sup> Jahn, *Z. physik. Chem.*, **41**, 257 (1902).

<sup>6</sup> Rothmund, *ibid.*, **69**, 523 (1909).



Comparing this with Equation 7, which depends on statistical principles, we see that the difference in the heats of solution of ether in two solutions of sodium chloride is directly proportional to the difference of the ion concentrations in the solutions.

Since, however, we are dealing with thermodynamic properties, it would seem more correct to replace Equation 9 above by

$$RT \log \frac{\eta_1}{\eta_2} = \alpha_{2,4} a_2 + \alpha_{3,4} a_3 \quad (10)$$

the  $a$ 's denoting activities of the ions, and the subscripts 2 and 3 referring to sodium ion and chlorine ion, respectively. It will be noted that the "environmental" effects of the ions are now separated since on the basis of activity, there is no *a priori* reason for assuming them equal. Harned<sup>7</sup> has computed the individual activities of the ions of such salts as potassium, sodium and lithium chlorides, and has shown that the observed activities of these salts in solution agree closely with the values calculated from the separate activity coefficients of the individual ions given by the empirical equation

$$\log F_a = \alpha c - \beta c^m$$

where  $\alpha$ ,  $\beta$  and  $m$  are constants for the particular ion considered, and  $F_a$  is the activity coefficient of the ion at the concentration  $c$  of salt (gram-molecules per 1000 g. of solvent).

The following table contains the activities of the sodium and the chlorine ions in the solutions used by Thorne, calculated from the above formula. The revised values of the constants  $\alpha$ ,  $\beta$ ,  $m$  for each ion given by Harned in a more recent communication<sup>8</sup> have been employed.

TABLE III

CALCULATED ACTIVITIES OF THE SODIUM AND CHLORINE IONS			
NaCl per 100 g. of soln. G.	Moles of NaCl per 1000 g. of H <sub>2</sub> O	Na <sup>+</sup>	Activity of Cl <sup>-</sup>
1	0.1728	0.1334	0.1272
2	0.3492	0.2557	0.2381
4	0.7130	0.5040	0.4434
5	0.9006	0.6357	0.5466
6	1.092	0.7755	0.6490
8	1.487	1.086	0.8600
10	1.901	1.447	1.086
15	3.019	2.684	1.736

Subtracting the value of  $\alpha_{2,4} a_2 + \alpha_{3,4} a_3$  for the 1% solution of sodium chloride from the values corresponding to the other solutions, and equating the results to the values of  $(Q_1 - Q_n)$  obtained from Col. 2 of Table II, we obtain the following relations.

<sup>7</sup> Harned, *THIS JOURNAL*, **42**, 1818 (1920).

<sup>8</sup> Harned, *ibid.*, **44**, 252 (1922).

$$0.1223 \alpha_{2,4} + 0.1109 \alpha_{3,4} = 69.2$$

$$0.3706 \alpha_{2,4} + 0.3162 \alpha_{3,4} = 207$$

$$0.5023 \alpha_{2,4} + 0.4194 \alpha_{3,4} = 275$$

$$0.6421 \alpha_{2,4} + 0.5218 \alpha_{3,4} = 346$$

$$0.9526 \alpha_{2,4} + 0.7328 \alpha_{3,4} = 482$$

$$1.314 \alpha_{2,4} + 0.959 \alpha_{3,4} = 621$$

$$2.551 \alpha_{2,4} + 1.609 \alpha_{3,4} = 964$$

Solving these seven equations in  $\alpha_{2,4}$  and  $\alpha_{3,4}$  by the method of least squares, we obtain as the most probable values  $\alpha_{2,4} = -21.7$ ;  $\alpha_{3,4} = 671$ . Having regard to the admittedly approximate nature of the activity values used, no special significance need be attached to the negative sign of  $\alpha_{2,4}$ , as a small error in any of the data used might easily lead to a positive value of  $\alpha_{2,4}$  of the same order of magnitude as that given above. The result obtained would therefore appear to indicate that *the effect of the cation in the salting out of ether by sodium chloride is negligible compared with the effect of the anion.*

It is believed that the foregoing is the first quantitative treatment of the salting-out effect of an electrolyte from the standpoint of the activities of the individual ions of the salt in solution.

It is proposed to test the conclusions arrived at above by experiments similar to those of Thorne, replacing the sodium chloride by other salts, for solutions of which the individual activity values of the ions are also available.

### Summary

1. The heats of solution of ether in various solutions of sodium chloride have been calculated from Thorne's solubility data at 15° and 25°, making use of a relation between solubility, heat of solution, and temperature of the form of the van't Hoff isochore.

2. Statistical treatment of the phenomena of solution and precipitation leads to an expression for solubility, viz.,  $s = Ae^{Q/RT}$ , which is in agreement with the isochore relation mentioned above.

3. The salting-out effect on ether of sodium chloride has been examined insofar as the effect depends on the activities of the ions of the salt. It is shown that the relative specific influences of the cation and anion are  $-21.7$  and  $+671$ , that is the anion is the predominating factor in the process. A mode of further testing this result is indicated.

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[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF YALE UNIVERSITY]

**EQUILIBRIUM IN THE SYSTEM AMMONIA : MERCURIC CYANIDE**

BY S. R. BRINKLEY

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Mercuric cyanide is one of a limited number of salts which are exceedingly soluble in ammonia, and lower the vapor pressure of the latter to such an extent that they deliquesce in the vapor at common temperatures when the vapor pressure is comparatively low.<sup>1</sup> Such solutions of salts in ammonia have recently received considerable attention, chiefly on account of the possibility of using them to condense ammonia at relatively low pressures in the absence of water.<sup>2</sup>

In the present article the vapor pressures at 0° have been determined for the binary system, ammonia : mercuric cyanide over a range from 370 mm. to about 1600 mm.; and in the ternary system of these two substances and water the solubility curve at the same temperature has been determined.

**Vapor Pressures**

The method used for determining the vapor pressure was that described by Foote and Brinkley.<sup>3</sup> For the vapor pressure of the saturated solution this method with the variation described by Foote<sup>4</sup> was used.

For the system where the phases were solid and vapor, the method used was first to prepare a solution of the salt in ammonia by passing in the gas at high pressure. The pressure of ammonia was then lowered to 370 mm. and ammonia evaporated to constant weight. Afterwards the higher pressures where these were the only phases, were used. It was found that reliable results were not obtained by the direct passage of ammonia at low pressures over mercuric cyanide, because of the time involved in reaching equilibrium in the solid phase transformation.

The mercuric cyanide was the purest that could be obtained and was recrystallized and dried until it showed no trace of moisture. Analysis showed it to contain no appreciable amount of any other substance.

The determinations were carried out at 0° only, since at higher temperatures the vapor pressure of the solution rises very rapidly.<sup>5</sup>

Table I shows the results of the vapor-pressure determinations. Several

<sup>1</sup> Franklin and Kraus, *Am. Chem. J.*, **20**, 820 (1898); *ibid.*, **23**, 300 (1900).

<sup>2</sup> Foote and Hunter, *THIS JOURNAL*, **42**, 69 (1920). Foote and Brinkley, *ibid.*, **43**, 1018 (1921). Davis, Olmstead and Lundstrum, *ibid.*, **43**, 1575, 1580 (1921).

<sup>3</sup> Foote and Brinkley, *Ref. 2*.

<sup>4</sup> Foote, *THIS JOURNAL*, **43**, 1031 (1921).

<sup>5</sup> Bradley and Alexander, *ibid.*, **34**, 15 (1912), erroneously reported mercuric cyanide to be among those substances which deliquesce in ammonia gas at ordinary temperatures and a pressure of one atmosphere.

samples were used to eliminate errors as far as possible. Corrections were made in weights for the changed gas content of the absorption tube, and the barometric readings were corrected for temperature. Col. 1 gives the observed vapor pressure of the system whose ammonia content is shown in Cols. 2 and 3. Col. 4 shows the percentage of the pressure of pure ammonia, exhibited by the solutions. The vapor pressure of ammonia at  $0^\circ$  is that determined by Keyes and Brownlee.<sup>6</sup> The data of Cols. 3 and 4 are of no significance when both solid and liquid phases are present and are therefore omitted from the table. Since this system is univariant, both composition of solution and vapor pressure are constant at the temperature of the experiment.

In the first part of the table the system was that in which no liquid phase was present. The composition of the solid was found to be constant over a wide range of pressures of ammonia and, moreover, to agree within experimental limits with that required by the formula,  $\text{Hg}(\text{CN})_2 \cdot 2\text{NH}_3$ . In the second part the data are for the system when varying amounts of solid were present with the saturated solution and vapor. The vapor pressure was found to be constant. The last part of the table shows the data for the unsaturated solution.

TABLE I  
VAPOR PRESSURES, AMMONIA:MERCURIC CYANIDE  
 $T = 0^\circ$   $P_{\text{NH}_3} = 3255$  mm.

P	Wt.-% $\text{NH}_3$	Mol.-% $\text{NH}_3$	$\frac{100 p}{P_{\text{NH}_3}}$	P	Wt.-% $\text{NH}_3$	Mol.-% $\text{NH}_3$	$\frac{100 p}{P_{\text{NH}_3}}$
I. Phases: $\text{Hg}(\text{CN})_2 \cdot 2\text{NH}_3$ and vapor.				II. Phases: $\text{Hg}(\text{CN})_2 \cdot 2\text{NH}_3$ , saturated solution vapor			
369	11.75	66.40	..	1053	16.57	...	..
556	11.63	...	..	1071	16.79	...	..
753	11.56	...	..	1067	18.35	...	..
993	11.59	...	..	1073	18.94	...	..
...	...	...	...	1065	19.30	...	..
...	...	...	..	1066	20.21	...	..
III. Phases: solution and vapor							
1067	20.72 <sup>a</sup>	79.34	32.8	1362	23.40	81.92	41.8
1098	20.93	79.71	33.7	1445	24.33	82.66	44.4
1200	21.87	80.57	36.9	1536	25.20	83.36	47.2
1257	22.36	81.02	38.6	1615	26.10	83.80	49.6

<sup>a</sup> Extrapolated value.

Fig. 1 shows these results graphically. The nearly vertical straight line shows the variable vapor pressure under which the solid  $\text{Hg}(\text{CN})_2 \cdot 2\text{NH}_3$  can exist. The slight deviation from the vertical is due to experimental error. The horizontal line shows constant vapor pressure of the saturated solution in the univariant system, where there are three phases. The proportions between the solid and solution change as the amount of

<sup>6</sup> Keyes and Brownlee, *THIS JOURNAL*, **40**, 35 (1918).

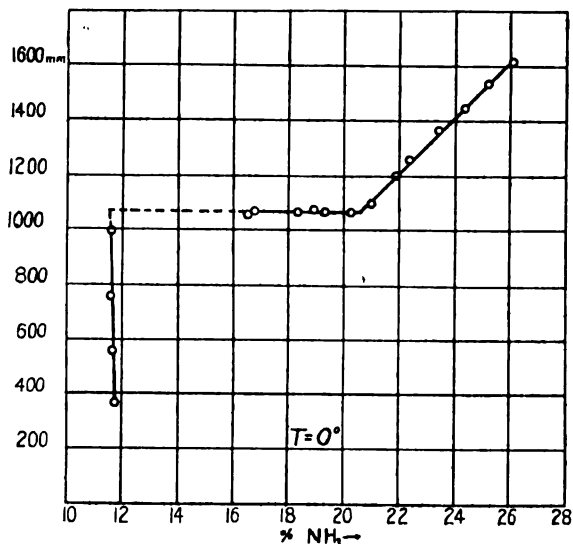


Fig. 1.

ammonia in the system increases. The ascending line shows the vapor pressures of the unsaturated solution. The point of intersection of the horizontal line and the vapor-pressure curve of the solution gives the composition of the saturated solution.

### Solubility

The vapor-pressure method was not suitable for determining the possible existence of other solid addition products, since at the low pressures involved there was considerable doubt of having reached equilibrium in the solid phase transformation, even after long passage of ammonia.

Recourse was therefore had to a solubility method for the investigation of this field. The aqueous solution of ammonia and mercuric cyanide was admirably adapted for this purpose, since in the dilute solutions very low partial pressures of ammonia could be obtained. If no solid hydrated addition product between mercuric cyanide and water could exist at  $0^\circ$ , the solid separating from solution would necessarily have the same composition as if it were in equilibrium with dry ammonia at this temperature, and a pressure of ammonia gas equal to its partial pressure in the aqueous solution. The solubility curve at  $0^\circ$  for the ternary system ammonia : mercuric cyanide : water was therefore determined.

These determinations were carried out in glass-stoppered bottles which were shaken in an ordinary solubility tank. In all cases the solutions were prepared at higher temperatures, taking care that the last trace of

solid was in solution. They were then brought to equilibrium at 0° by long shaking in the solubility tank.

The samples for analysis were withdrawn through a tube containing a plug of glass wool into a weighed specimen tube. The precautions previously described<sup>3</sup> were used to minimize errors. Ammonia was determined in the usual way by adding a measured excess of standard hydrochloric acid and titrating the excess by means of standard ammonia solution, using congo red as indicator. Previous determinations had shown that the presence of mercuric cyanide did not affect the accuracy of the method. Mercuric cyanide was determined by precipitating mercuric sulfide in hydrochloric acid solution with hydrogen sulfide, and drying to constant weight at 110°, previous tests having shown this to give accurate results.

The composition of the solid phase was determined by Schreinemakers' method<sup>7</sup> of residues. The solubility results are given in Table II. The solubility of mercuric cyanide in pure liquid ammonia was obtained by extrapolation from the vapor-pressure data.

TABLE II  
SOLUBILITY. AMMONIA: MERCURIC CYANIDE: WATER  
 $T=0^\circ$

Solution		Residue		Solid phase
Wt.-% $\text{Hg}(\text{CN})_2$	Wt.-% $\text{NH}_3$	Wt.-% $\text{Hg}(\text{CN})_2$	Wt.-% $\text{NH}_3$	
6.31	None	Not analyzed		$\text{Hg}(\text{CN})_2$
8.46	.43	89.22	.05	
11.66	1.09	92.58	.55	
11.69	1.06	89.24	2.66	
9.40	2.06	83.95	5.74	
9.44	2.74	84.05	5.82	$\text{Hg}(\text{CN})_2 + \text{Hg}(\text{CN})_2 \cdot \text{NH}_3$
10.32	4.08	85.11	6.14	
15.43	6.82	85.31	6.04	
17.51	7.67	87.65	6.24	
19.31	8.25	84.69	6.36	
24.68	9.40	84.37	6.48	$\text{Hg}(\text{CN})_2 \cdot \text{NH}_3$
25.41	9.50	81.75	9.33	
25.41	9.55	79.92	9.71	
25.52	9.50	80.92	10.34	
24.04	11.23	79.00	11.58	
23.40	12.59	77.73	11.84	$\text{Hg}(\text{CN})_2 \cdot 2\text{NH}_3$
24.46	16.87	76.80	12.56	
43.57	22.09	84.04	12.31	
66.10	21.51	86.03	12.11	
79.30 <sup>a</sup>	20.70	...	...	

<sup>a</sup> Extrapolated from v. p.

<sup>7</sup> Schreinemakers, *Z. physik. Chem.*, **55**, 73 (1906).

The solubility curve is shown in Fig. 2. Along the curve AB mercuric cyanide is the solid phase, along the curve BC the solid is of the composition  $\text{Hg}(\text{CN})_2 \cdot \text{NH}_3$ , and along the curve CD the solid is  $\text{Hg}(\text{CN})_2 \cdot 2\text{NH}_3$ . At the univariant point B the two solids  $\text{Hg}(\text{CN})_2$  and  $\text{Hg}(\text{CN})_2 \cdot \text{NH}_3$  are in equilibrium with a solution of fixed composition for fixed temperature; and at the univariant point C, the solid phases are  $\text{Hg}(\text{CN})_2 \cdot \text{NH}_3$  and  $\text{Hg}(\text{CN})_2 \cdot 2\text{NH}_3$ .

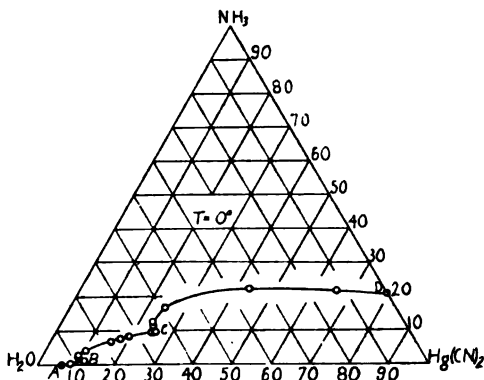


Fig. 2.

The addition product  $\text{Hg}(\text{CN})_2 \cdot 2\text{NH}_3$  was described by Franklin and Kraus<sup>8</sup> as obtained when a solution of mercuric cyanide in liquid ammonia was allowed to evaporate.

Varet<sup>9</sup> mentioned the existence of the two addition products and also of two hydrated addition products of the composition  $\text{Hg}(\text{CN})_2 \cdot \text{NH}_3 \cdot \frac{1}{2}\text{H}_2\text{O}$ ; and  $\text{Hg}(\text{CN})_2 \cdot 2\text{NH}_3 \cdot \frac{1}{2}\text{H}_2\text{O}$ .

The conditions under which he worked were not well defined. Moreover the physical appearances of the hydrated and unhydrated products as described by him are essentially the same. Since these addition products rapidly lose ammonia when exposed to the air, it would obviously be difficult to obtain them completely free from solution without some decomposition. The amount of water required to satisfy the above formulas is very small and could readily be explained as due to failure to free his solids completely from solution.

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In this investigation no hydrated products were obtained even from the most dilute solutions. It is evident that at 0° the two addition products described are the only ones capable of separating in the solid phase from the solution; and therefore are the only solid addition products capable of existence.

### Discussion of Results

Reference to Table I shows that the vapor pressures of the solutions of different composition vary greatly from those required by Raoult's law. In Cols. 3 and 4, respectively, the molecular percentage of ammonia and the relation  $100 p/P_{\text{NH}_3}$  are shown. According to Raoult's law these values should be identical.

Footnote and Hunter<sup>2</sup> for the system ammonia: ammonium thiocyanate,

<sup>8</sup> Franklin and Kraus, *THIS JOURNAL*, 29, 49 (1907).

<sup>9</sup> Varet, *Bull. soc. chim.*, [3] 6, 220 (1891); *Compt. rend.*, 109, 903 (1889), and 112, 313 (1891).

and Foote and Brinkley<sup>2</sup> for the system ammonia: ammonium nitrate concluded that the great deviation was due partly to the formation of addition products in solution, and partly to electrolytic dissociation. Since mercuric cyanide is not appreciably ionized in ammonia solution<sup>10</sup> and since solid addition products have been shown to exist at 0°, the divergence here may to a very large extent be attributed to compound formation. On this basis the average composition of the compound in solution may be calculated by the Callendar formula used in the above mentioned articles:

$$\frac{p_0 - p}{p_0} = \frac{n}{N - an + n} . \text{ Here } p_0 \text{ and } p \text{ represent the vapor}$$

pressures of ammonia from the pure solvent and the solution respectively;  $N$  the molecules of solvent;  $n$  the molecules of solute; and  $a$  the number of molecules of solvent combined with one molecule of solute. In Table III the values of  $a$  have been calculated for several mercuric cyanide solutions.

TABLE III  
MOLECULES OF SOLVENT ( $a$ ) COMBINED WITH SOLUTE  
 $T=0^\circ$

Mol. per cent. of ammonia	$a$	Mol. per cent. of ammonia	$a$
83.80	4.18	81.02	3.64
82.66	3.97	79.34	3.35

Comparison with the results of Foote and Brinkley<sup>2</sup> shows that in the extent of compound formation with ammonia the salts stand in the following order: ammonium thiocyanate, mercuric cyanide, ammonium nitrate. This is shown by the fact that for solutions of the same molecular concentration the abnormality in the depression of the vapor pressure is greatest for ammonium thiocyanate and least for ammonium nitrate.

By interpolation from the data of Davis, Olmstead, and Lundstrum<sup>2</sup> and conversion to molecular percentages, it is found that at 0° the solution of lithium nitrate in ammonia shows a vapor pressure of 290 mm., when the molecular percentage of ammonia is 69.03. For the same concentration the ammonium thiocyanate solution shows a pressure of 270 mm.,<sup>3</sup> and the ammonium nitrate solution 665.<sup>3</sup> The values of  $a$  for these solutions are: ammonium thiocyanate,  $a = 2.14$ ; lithium nitrate,  $a = 2.12$ ; ammonium nitrate,  $a = 1.97$ , as derived from the vapor-pressure data. The solutions in which the vapor-pressure lowering is greatest, show the compound formation to the greatest extent.

The molar solubility of mercuric cyanide in ammonia is not as great as in the case of the other salts mentioned, and the vapor pressure of the saturated solution is considerably higher than for any of these. The rate of absorption of ammonia by mercuric cyanide is also slower and a much greater time is necessary for reaching equilibrium. Hence it probably

<sup>10</sup> Franklin and Kraus, *Am. Chem. J.*, 23, 277 (1900); *THIS JOURNAL*, 27, 197 (1905).



would not be as satisfactory an absorbent for ammonia for practical use as those described by Foote and Hunter,<sup>2</sup> Foote and Brinkley<sup>2</sup> and Davis, Olmstead and Lundstrum.<sup>2</sup>

### Summary

1. The vapor-pressure curve at 0° for the system ammonia:mercuric cyanide has been determined from 369 to 1615 mm.
2. The solubility curve of the ternary system ammonia:mercuric cyanide:water has been determined at 0°.
3. The vapor pressures of the solutions are far below those required by Raoult's law.
4. The solid addition products,  $\text{Hg}(\text{CN})_2 \cdot \text{NH}_3$  and  $\text{Hg}(\text{CN})_2 \cdot 2\text{NH}_3$ , have been isolated and have been shown to be the only ones formed at 0°.

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## THE CONSTITUTION OF METALLIC SUBSTANCES

BY CHARLES A. KRAUS

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### I. Introduction

Recent advances in our knowledge of the structure of the atoms and of crystalline substances have made it possible to render a fairly satisfactory account of the constitution of salts and of many non-metallic compounds. The constitution of metallic elements and metallic compounds, however, remains almost as obscure as heretofore. Indeed, few writers have ventured to hazard a guess as to the nature of these interesting substances.

Approximately 80% of the known elements are metallic in the free state, and all compounds between distinctly metallic elements are metallic. In addition, many compounds between metallic and non-metallic elements are likewise metallic. The metals thus include a large number of important substances. The study of metallic substances has received little attention, particularly from the chemical point of view. It is only recently that methods have been developed as a result of which we now have information relative to the composition of metallic compounds. Even now, many simple systems have not been systematically studied, while the more complex systems have scarcely been touched upon except in a few instances. The physical and chemical properties of metallic compounds are little known even from a qualitative standpoint. Data relative to the energy changes accompanying the formation of metallic compounds are very meager. It is apparent that at the present time the metals constitute a great field which remains practically undeveloped.

Before proceeding to a discussion of the constitution of metallic sub-

stances, it will be advantageous to consider, briefly, the metallic state of matter, in general. The uniform occurrence of certain properties in different metallic substances indicates some common feature underlying their constitution. According to modern views, the metals owe their characteristic properties chiefly to the negative electrons which are free to move within the body of the metal. Much of our knowledge relative to the existence of free negative electrons in metals is derived from indirect evidence. The most direct evidence as to the existence of negative electrons in metallic elements has been obtained from a study of solutions of the alkali metals in liquid ammonia. This solvent constitutes the only non-metallic medium in which metals are soluble. Solutions in ammonia, therefore, constitute the only means we have for obtaining an insight into the influence of concentration on metallic properties. In what follows it will be necessary to draw largely on the results obtained from the study of solutions in this solvent.

The properties of a given system, as regards its chemical behavior, depend largely upon the tendency which the constituent elements possess for combining with negative electrons to form stable complexes. Electronegative elements owe their characteristic property of functioning as anions to the fact that they form stable complexes with one or more negative electrons. This union of the negative electron with an electronegative element or group of elements is a relatively stable one, and persists throughout the various compounds in which this element or group of elements occurs. It is only with great difficulty that these complexes may be broken down. Since, under these conditions, the negative electrons are firmly attached to atomic groups, they possess freedom of motion only insofar as these groups, as a whole, are capable of moving under given conditions. Metallic properties are therefore lacking in such compounds. Only such substances may be expected to exhibit metallic properties as do not contain sufficient electronegative elements to engage the negative electrons supplied by the more electropositive constituents, or, otherwise, in which uncombined electronegative elements are lacking.

Any element or group of elements which is capable of forming a stable complex with the loss of one or more negative electrons possesses, in a sense, metallic properties. Whether a given system containing such groups will be metallic depends upon whether or not other more electronegative constituents are present to combine these electrons. The smaller the affinity of an element or group of elements for the negative electron, the more electropositive will the element or group appear, and the more readily will it enter into reaction with more electronegative elements.

According to this view, the metallic elements are to be looked upon as salt-like substance in which the negative electron appears as electronegative constituent. Chemical reactions in which these elements are con-

cerned consist essentially in a combination of the negative electron with an electronegative element or group of elements. The energy effects accompanying such reactions are largely due to the reaction taking place between the negative electron and the electronegative constituent to form a negative ion. This will be the more true, the more electropositive the metallic constituent and the more electronegative the electronegative constituent. Compounds between strongly electronegative and electropositive constituents, therefore, should invariably form salts or salt-like substances. On the other hand, compounds between strongly electronegative elements and only weakly electropositive elements may be expected to yield substances in which the salt-like properties are subordinate.

It should further be borne in mind that the properties of a substance depend upon its state. This is particularly true of metallic properties. These properties are extremely sensitive to a slight change in the environment of the substance. For example, the specific resistance of a metal is very sensitive to change of temperature, pressure and other factors. The metallic state of an element is particularly dependent upon its concentration. This will be clear when it is recalled that the vapors of metallic elements are throughout non-metallic. Thus, mercury vapor under ordinary conditions is a non-conductor; and even at high temperatures and at densities comparable with those of the metal, mercury vapor is a very poor conductor.<sup>1</sup> In the case of electrolytes, it is well known that the properties are dependent upon concentration, particularly when dissolved in solvents of low dielectric constant. While the salts in the pure state exhibit a high equivalent conductance, dissolved in solvents of low dielectric constant, such salts exhibit an extremely low conducting power. So, also, salt vapors exhibit only a very low conductance. We may conclude, therefore, that the properties of salt-like substances, and the metals may be included in this class, will vary largely as a function of concentration. That this important fact should have escaped observation in the case of metals is not surprising, since, as a rule, metals are not soluble in non-metallic liquids.

It is unsafe to draw conclusions relative to the constitution of chemical compounds from their behavior in the solid state, for it is well known that in this state the various elements of the compound exist under the action of forces which tend to arrange them in a compact and orderly manner, more or less irrespective of the nature of the forces which may be operative under other conditions. It would appear that the constitution of compounds could be successfully studied only in the liquid or vapor state at relatively low concentrations, where interacting forces, except such as are primarily concerned in forming the compounds themselves, are practically eliminated. If, therefore, we wish to determine

<sup>1</sup> Strutt, *Phil. Mag.*, 4, 596 (1902).

the constitution of metallic substances, it will be necessary to obtain these substances in a non-crystalline state at low concentrations. In the case of strongly electropositive elements, it is to be expected that the properties will vary gradually from those of a metal to those of an electrolyte or salt, as the concentration of the metal decreases. At very low concentrations, assuming that no other substances are present, it is to be expected that the metallic atom will be a neutral complex possessing no metallic properties. If, on the other hand, an ionizing medium were present, we should expect certain properties of the electronic compound to persist. Since salts are ionized in electrolytic solvents at low concentrations, we should expect the metals to be ionized under similar conditions, and the ionization should vary as a function of the concentration in a similar manner. It is possible, and indeed probable, that at very low concentrations the negative electron will no longer possess that freedom of motion which is characteristic of the metallic state. For, even though the solvent molecules were incapable of forming a stable complex with the negative electron, it is to be expected that, owing to the action of their field, the electrons would be associated with the solvent molecules with a consequent reduction of their mobility. This is known to be the case in gaseous systems, where the negative electron may readily be formed by means of external radiations. At ordinary pressures, the mobility of the negative electron is as low as, or even lower than, that of positive ions. It is only at low concentrations of the gas that the mobility of the negative electron becomes comparable with that which might be expected of free electrons. It may be expected that in many instances the negative electron will form more or less stable complexes with the solvent medium, in which case, practically, salts will be formed. Such systems will not be metallic at high concentrations.

The question to be determined is this: what elements are capable of forming stable complexes with negative electrons? Let us suppose, for example, that both sodium and tin were soluble in a given solvent. What would be the properties of such a solution at low concentrations? While in the pure state, tin is a metallic element which presumably furnishes free negative electrons in this state; on the other hand, it is well known that tin forms many compounds which are relatively non-salt-like in property.<sup>2</sup> Is it not conceivable, therefore, that in such a mixture tin would associate itself with the negative electron to form a stable complex, namely, a tin anion? It is well known that sodium and tin form a series of relatively stable compounds. Assuming the existence of a solvent in which these compounds were soluble, we may inquire as to what would be the properties of these solutions. From what has already been said, it is clear that, whatever the nature of these compounds may be,

<sup>2</sup> For example, stannic chloride.

it is not to be expected that dilute solutions of such compounds will be metallic. Even solutions of the alkali metals themselves, in the presence of a non-reactive solvent, in other words, a solvent with which the alkali metals form no compounds, lose, to a large extent, their characteristic metallic properties at low concentrations. We are led to conclude that solutions of metallic compounds at low concentrations will exhibit purely non-metallic properties, or, possibly, salt-like properties, since it is conceivable, or even probable, that the more electronegative metallic elements may form stable complexes with negative electrons supplied by the more electropositive metals. We may inquire whether there are available any facts indicating that compounds of strongly electropositive elements with less electropositive metallic elements are salt-like in character. As will be shown below, numerous metallic compounds exist whose properties are fully in harmony with this view.

## II. The Negative Valences of Metallic Elements

According to present views regarding the structure of matter, elementary substances (excepting elements of the argon group) may be expected to exhibit either electropositive or electronegative valence. The conception has frequently been employed in accounting for the structure of compounds among non-metallic elements but appears not to have been extended to compounds among metallic elements. *A priori*, there is no reason why an element which ordinarily exhibits a fairly strong electropositive valence might not be expected to exhibit, likewise, a fairly strong electronegative valence. This is unquestionably the case with hydrogen which, in combination with strongly electronegative elements, appears to be positively charged or, at any rate, is associated with the positive ion, while in the hydrides of the strongly electropositive elements it is negatively charged.<sup>3</sup>

The normal compounds of the strongly electropositive elements with sulfur, selenium and tellurium are non-metallic. On the other hand, similar compounds with arsenic, antimony and bismuth are metallic. The greater the atomic number of an element, and the farther it lies removed from the seventh group of elements, the more pronounced are the metallic properties of its compounds with more electropositive elements. So, the compounds of the alkali metals with antimony and bismuth are more metallic than those with arsenic and phosphorus. Similarly, the compounds of sodium with mercury and lead are more distinctly metallic than those with bismuth and tellurium. Sodium forms with antimony the compound  $\text{Na}_3\text{Sb}$ . There is no reason for believing that this compound differs essentially from the nitride  $\text{Na}_3\text{N}$ , or the phosphide  $\text{Na}_3\text{P}$ , on the one hand, or from the sulfide  $\text{Na}_2\text{S}$  or the telluride  $\text{Na}_2\text{Te}$ , on the other.

<sup>3</sup> Moers, *Z. anorg. Chem.*, 113, 179 (1920).

In the fourth group, lead and tin form stable compounds,  $\text{Na}_4\text{Pb}$  and  $\text{Na}_4\text{Sn}$ , in which these elements may be assumed to exhibit a negative valence of 4. It appears, then, that the elements of the sixth group exhibit a marked negative valence of 2, those of the fifth group of 3, and those of the fourth group of 4. The compounds in which the elements appear combined according to these proportions are relatively very stable, as is indicated by their melting-point diagrams, and the heat effects accompanying their formation. While the compounds of the heavier metals of the fourth and fifth groups are metallic, those of the sixth groups are non-metallic. It follows that the compounds of the elements of the various groups are essentially of the same nature. In other words, the property of metallicity does not involve a fundamental difference between the structure of such compounds and the structures of non-metallic compounds.

The question may be raised: if the more electronegative elements in metallic compounds are, in fact, negatively charged, why have we no data which indicate the existence of such negative ions? The answer to this question is obvious; the compounds in question have not been studied under conditions in which such properties might be expected to be disclosed. As we shall see below, under suitable conditions, compounds of this type yield conclusive evidence of the existence of negative ions of metallic elements.

### III. Complex Negative Ions of Metallic Elements

A difficulty which confronts any theory of the constitution of metallic compounds lies in the multiplicity of compounds derivable from a single pair of metallic elements. Thus sodium and tin form the compounds  $\text{Na}_4\text{Sn}$ ,  $\text{Na}_2\text{Sn}$ ,  $\text{Na}_3\text{Sn}$ ,  $\text{NaSn}$  and  $\text{NaSn}_2$ . Writers on this subject have been misled in that they have looked upon the compositional formulas as indicative of the constitution of these compounds. When such writers have expressed an opinion as to the nature of such compounds they have, as a rule, been inclined to take the position that in these compounds the atoms are held together by forces essentially different from those operative in the case of non-metallic compounds.<sup>4</sup> Too much emphasis has been placed upon the proportions in which the various atoms combine. Apparently, no attempt has been made to discover to what extent the various atoms entering into metallic compounds exist in the same condition. In a compound of the type  $\text{NaSn}_2$ , for example, are all the tin atoms present in the same condition, in other words, are all the tin atoms of this compound equivalent; or do these compounds possess a definite structure in which the relation of tin atoms to the sodium atoms differs for different atoms?

The argument will perhaps be clearer when it is recalled that the tendency

<sup>4</sup> Tammann, "Lehrbuch der Metallographie," Leopold Voss, 1914, p. 230.

of relatively electronegative atoms to form stable negatively charged complexes is very pronounced. Thus, we have such complexes as the sulfate ion, nitrate ion, chlorate ion, perchlorate ion, etc. In these complexes the elements are arranged in a definite manner under all conditions, whether in the solid or the fused state or in solution. Furthermore, the nature of these complexes is not materially affected by the nature of the electropositive constituent with which they appear combined. Very striking, for example, is the trinitride ion,  $N_3^-$ , in which three nitrogen atoms appear combined to form a stable, singly charged complex anion. This tendency of electronegative elements to form complexes is one much more common than has hitherto been suspected. This is particularly true of complexes in which a single element is concerned. The most familiar example of this type of complex anion is the tri-iodide ion. It has been shown that it is a general property of the iodide ion to associate with itself two additional atoms of iodine to form a relatively stable complex. In solution, an equilibrium exists between the simple iodide ion and the complex ion. In the solid state the iodides include  $MI$ ,  $MI_3$ ,  $MI_5$ ,  $MI_7$  and  $MI_9$ , where  $M$  is a univalent element.<sup>5</sup> Among other elements which exhibit a similar tendency to form complex ions, only the complex sulfide ion has been studied extensively.<sup>6</sup> It has been shown that the normal sulfide ion takes up additional sulfur to form a series of complex anions,  $S_2S^{--}$ ,  $S_3S^{--}$ ,  $S_4S^{--}$ ,  $S_5S^{--}$ . Thus far, the complex sulfides have been studied only in aqueous solution. However, this property of the sulfide ion to form complexes with additional sulfur atoms is not restricted to aqueous solutions, but is one common to sulfides in numerous solvents. There is evidence indicating that selenium and tellurium similarly form complex ions, although only the complex telluride ion has been studied in some detail in aqueous solution.<sup>7</sup> May we not infer that other elements than those of the sixth and seventh groups exhibit a pronounced tendency to form complex anions? This hypothesis would account, for the most part, for the large number of compounds formed from a single pair of metallic elements.

We may, indeed, proceed one step further and suggest that the atoms in an elementary substance do not all function in the same manner. Is it not conceivable that many elements are, in effect, compounds in which certain atoms act electropositively and others electronegatively? This would account for many of the properties of the less distinctly electropositive metallic elements.

<sup>5</sup> Abel and Halle, Abegg's "Handbuch der anorganischen Chemie," S. Hirzel, 1913, IV, 2, p. 432.

<sup>6</sup> Küster and Heberlein, *Z. anorg. Chem.*, **43**, 53 (1905); Küster, *ibid.*, **44**, 431 (1905); **46**, 113 (1905).

<sup>7</sup> Tibbals, *THIS JOURNAL*, **31**, 902 (1909).

#### IV. The Nature of Metallic Substances Dissolved in Liquid Ammonia

One of the great difficulties encountered in the study of the nature of metallic substances lies in the fact that these substances can be obtained only in the pure state or dissolved in other metallic substances. It is difficult, therefore, to determine to what extent the properties of the resulting system are due to a given constituent. As has already been pointed out, the state of a system is largely dependent upon its concentration. If the concentration of a given constituent may be altered by the introduction of a second constituent whose properties differ markedly from those of the first, then a study of the manner in which the properties of the first constituent vary as a function of concentration yields important information as to the nature of the substance in question. Thus far, only a single class of solvents has been discovered in which metallic substances are more or less generally soluble, namely, liquid ammonia and the amines. In addition to the alkali metals and the metals of the alkaline earths, liquid ammonia dissolves a number of metallic compounds.<sup>8</sup>

Let us consider, first, the properties of metallic elements dissolved in liquid ammonia. It has been conclusively shown that solutions of the strongly electropositive elements in liquid ammonia exhibit properties intermediate between those of metals and electrolytes, the properties varying continuously as a function of concentration.<sup>9</sup> At very low concentrations, a solution of an element is virtually a solution of a salt, for in these solutions the positive ion exhibits all the properties characteristic of an ion of a normal salt, while the negative ion exhibits many properties similar to those of anions of typical electrolytes. The conducting power of the negative ion, for example, is comparable with that of ordinary negative ions. In other respects, the properties of the negative ion in dilute solutions of the metals in ammonia differ materially from those of typical electronegative ions in the same solvent. The chief difference lies in the fact that, in the typical anions, the negative electron is firmly associated with an electronegative element or group of elements, whereas in an ammonia solution of a metal the negative ion consists essentially of a negative electron rather loosely associated with ammonia molecules. The electrolytic character of different metallic elements is clearly exhibited in the ionization equilibria in ammonia solution. The conductance curves of solutions of the metals in ammonia at low concentrations are practically identical in form with those of typical salts of the same metals in this solvent. Assuming the degree of ionization to be measured by the ratio of the equivalent conductance at a given concentration to the limiting value which the equivalent conductance approaches at low concentration, the ionization of typical metals in liquid ammonia is practically the same as that of the correspond-

<sup>8</sup> Kraus, *THIS JOURNAL*, 29, 1557 (1907).

<sup>9</sup> Kraus, *ibid.*, 43, 749 (1921); 36, 864 (1914); 30, 1323 (1908).



ing salts in the same solvent. Unquestionably, in solutions of metals in liquid ammonia we are dealing with equilibria similar to those in solutions of the corresponding salts.

Indeed, we not only have equilibria between different metals in ammonia solution; we also have equilibria between the metals and typical salts in this solvent. Solutions of metals in the presence of salts of other metals do not yield reaction products when these products are soluble. When an insoluble product may be formed, however, this product is precipitated. Thus, metallic calcium reacts with potassium chloride metathetically according to the reaction equation  $2\text{KCl} + \text{Ca} = \text{CaCl}_2 + 2\text{K}$ , insoluble calcium chloride being precipitated and metallic potassium remaining in solution. If a salt of a metal insoluble in ammonia is added to a solution of a metal, the insoluble metal is precipitated. Thus  $\text{AgI} + \text{Na} = \text{NaI} + \text{Ag}$ , silver being precipitated. In many instances, however, the precipitated metal itself is capable of forming anions, in which case a compound of the two metals is precipitated. Thus  $\text{BiCl}_3 + 6\text{Na} = 3\text{NaCl} + \text{Na}_3\text{Bi}$ , the bismuthide being precipitated as a metallic compound. The behavior of solutions of the metals in ammonia is similar to that of solutions of salts. We may conclude, therefore, that at low concentrations the metals are, in fact, salt-like in character.

At higher concentrations, certain properties of the metal solutions begin to diverge markedly from those of solutions of non-metallic substances. This change in the properties of solutions of metallic substances is to be ascribed, primarily, to the fact that the negative electron is freed from its association with atoms or groups of atoms at high concentrations. As a consequence, the conductance of solutions at higher concentrations becomes sufficiently great to impart to them distinctly metallic properties. There is nothing to indicate that the nature of the metal in solution has been greatly altered at higher concentrations. In other words, at higher concentrations, the electropositive constituent continues to exist as a positive ion, while the electronegative constituent yields free negative electrons as a result of which the metallic properties appear. What portion of the total number of negative electrons in a metallic element at higher concentrations actually takes part in the conduction process cannot be stated. It is not unlikely that, in the alkali metals, the greater portion of the negative electrons are in a condition in which they are capable of carrying the current.

If the metallic elements themselves are salt-like in character, then there is all the more reason for believing that metallic compounds likewise are salt-like, particularly, compounds in which one of the elements is strongly electropositive and the other strongly electronegative. Here, again, solutions in liquid ammonia supply definite information relative to the constitution of metallic substances. Various compounds of the alkali

metals with the heavy metals of the fourth, fifth and sixth groups are very soluble in liquid ammonia. In general, the solutions of such metallic compounds are characteristically colored, but they exhibit no marked metallic properties except, possibly, at very high concentrations.<sup>8</sup> So, for example, concentrated solutions of a compound of sodium and lead exhibit a distinct metallic luster, somewhat of a violet tint.

The important question to be answered is: what is the nature of these metallic compounds in solution? In the first place, it is to be noted that the process of solution and precipitation of such metallic compounds is a reversible one and is accompanied by a relatively small energy change, which indicates that, if ammonia is associated with these compounds in solution, such association is purely of a secondary nature. There is nothing to indicate that the compounds in solution differ materially in nature from the same compounds in the solid state. If metallic compounds are salt-like in character, we should expect that in solution, at low concentrations, the more electropositive element would be present as a normal cation and the electronegative element as an anion. By analogy, we should expect the metals of the sixth group to form divalent anions, of the fifth group trivalent anions, and of the fourth group quadrivalent anions. Whether the metals of the third group form quinquivalent anions is uncertain, since only thallium forms a soluble compound, and its solubility is so low that its nature cannot readily be determined.<sup>10</sup> It is possible, too, that the negative valence of a metallic anion may be variable, just as the positive valence of the same metal is often found to be variable. This tendency to variation in electronegative valence, if it exists, might be expected to become more pronounced as the element becomes more electropositive.

Whether a solution of a compound is an electrolyte is readily determined by subjecting it to electrolysis. Sodium reacts with metallic lead in liquid ammonia, giving a solution containing approximately 2.25 atoms of lead per atom of sodium.<sup>11</sup> Leaving aside for the moment the precise nature of the compound in question, we should expect that, if the lead is associated with the anion, 2.25 atoms of lead would be precipitated on the anode when one equivalent of electricity passes through the solution. That solutions of the sodium-lead compounds are electrolytes was shown by Kraus<sup>9</sup> and later by Posnjak and by Smyth.<sup>11</sup> In these solutions approximately 2.25 atoms of lead are precipitated on the anode, corresponding to the mean composition of the solution. Without question, lead is present in these solutions as a negative ion. That antimony is present as an anion in liquid ammonia was shown by Peck,<sup>12</sup> although

<sup>10</sup> Unpublished observations by Mr. H. F. Kurtz in this Laboratory.

<sup>11</sup> Smyth, *THIS JOURNAL*, 39, 1299 (1917).

<sup>12</sup> Peck, *ibid.*, 40, 335 (1918).

owing to the difficulty of precipitating the antimony on the anode in coherent form, the results of electrolysis do not agree with the composition of the solution as satisfactorily as in the case of lead.

The nature of the complexes formed between sodium and tellurium in liquid ammonia solution has been studied in some detail in this Laboratory.<sup>13</sup> Briefly, when metallic tellurium is introduced into a solution of sodium in liquid ammonia, reaction takes place with great facility, resulting in the formation of the normal telluride,  $\text{Na}_2\text{Te}$ , which is largely precipitated as a white, slightly crystalline non-metallic substance. This telluride is slightly soluble, and, in the presence of metallic tellurium, reacts further to form complex tellurides. In the first stage of the reaction the compound  $\text{Na}_2\text{Te}_2$  is formed, the composition of the solution in equilibrium with the normal telluride corresponding to this formula. In the presence of excess tellurium, the normal telluride goes completely into solution, forming a complex which probably has the composition  $\text{Na}_2\text{Te}_4$ , since this corresponds very closely with the mean composition of the solution at higher concentrations.

The properties of the complexes formed depend upon the amount of tellurium associated with the anion. The normal telluride, as already mentioned, is a non-metallic substance, only slightly soluble in liquid ammonia. The compound  $\text{Na}_2\text{Te}_2$  is extremely soluble in liquid ammonia and forms a deep violet-blue solution. When precipitated from solution, this complex exhibits metallic properties. The compound  $\text{Na}_2\text{Te}_4$  is likewise extremely soluble, forming a deep red solution in liquid ammonia, and this compound, also, is metallic when precipitated. It is interesting to note that the introduction of additional tellurium into the anion complex converts the normal non-metallic telluride to a metallic substance. At very low concentrations, the proportion of tellurium present in a solution in equilibrium with metallic tellurium falls below the value corresponding to the formula,  $\text{Na}_2\text{Te}_4$ , but at high concentration the composition of the solution approaches a value corresponding to that of this compound very closely. It may be inferred that at low concentrations an equilibrium exists between two or more complexes; as, for example,  $\text{Na}_2\text{Te}_4$  and  $\text{Na}_4\text{Te}_3$ . This is not unexpected, since the ionization and possibly other fundamental properties of the compound undergo alteration as the concentration decreases. In this, the behavior of the compound does not differ materially from that of the corresponding complex sulfides and iodides in aqueous solution.

It remains to determine definitely the constitution of the complex telluride anion. This can be done by molecular-weight determinations only. While the determination of molecular weights at higher concentrations is very uncertain, owing to the fact that the laws of dilute solutions are

<sup>13</sup> C. Y. Chiu, *Dissertation*, Clark University, 1920.

not applicable and the laws governing the equilibria in such systems are unknown; by determining the apparent molecular weight at a series of concentrations and thus determining the manner in which this quantity varies as a function of the concentration, an inference may be drawn as to the probable complexity of the substance in solution. Such a study has been carried out in this Laboratory, as a result of which it appears that the anion carries two negative charges.<sup>14</sup> Presumably, the anion consists of a normal telluride ion  $\text{Te}^{--}$  associated with additional tellurium. There are thus in solution under various conditions the anions:  $\text{Te}^{--}$ ,  $\text{TeTe}^{--}$ , and  $\text{Te}_3\text{Te}^{--}$ . This view of the constitution of the complex telluride ion is in harmony with the accepted theory of the constitution of the complex sulfide ion.<sup>15</sup>

Peck<sup>12</sup> has shown that antimony forms a series of complex anions in liquid ammonia solution in the presence of a sodium ion. The initial compound here precipitated has the composition  $\text{Na}_3\text{Sb}$ , corresponding with the normal electronegative valence of antimony. It is interesting to note that, while the normal telluride is non-metallic, the normal antimonide is metallic. The normal antimonide is only slightly soluble in liquid ammonia. In the presence of excess antimony, the mean composition of the solution varies as a function of concentration. At a concentration 0.0049 *N* in sodium, the atomic ratio of antimony to sodium in solution is 1.198, differing thus very little from a proportion of one atom of antimony to one atom of sodium. At higher concentrations the proportion of antimony to that of sodium increases, reaching a maximum of 2.333 atoms of antimony per atom of sodium at a concentration 0.4347 *N*. At still higher concentrations, the proportion of antimony to sodium decreases slightly.

The complexity of the anion in the antimony solutions has not been determined, but it appears probable that the nature of the anion in antimony solutions does not differ materially from that of the corresponding ion in tellurium solutions. Accordingly, the antimony anion carries 3 negative charges, corresponding to those of the normal antimonide ion. Otherwise, it would be necessary to assume that the electronegative valence of antimony changes as a function of the proportion of antimony present in the solution. This assumption appears improbable. The highest atomic ratio in the antimony solutions corresponds to the formula  $\text{Na}_3\text{Sb}_4$ .

The ratio of sodium to lead in the lead solutions, as already stated, is approximately 2.25 atoms of lead per atom of sodium, and this ratio appears to be independent of the concentration. The normal plumbide is  $\text{Na}_4\text{Pb}$ . Unless the electronegative valence of lead changes, as additional

<sup>14</sup> E. H. Zeitfuchs, *Dissertation*, Clark University, 1921.

<sup>15</sup> Küster and Heberlein, Ref. 6.

lead is combined with the anion, the complex in solution corresponds to the formula  $\text{Na}_4\text{Pb} \cdot \text{Pb}_8$ .

In the accompanying figure the ratio of antimony to sodium is represented by Curve A, that of tellurium to sodium by Curve B, and that of sulfur to sodium in aqueous solutions by Curve C. The similarity of the curves is unmistakable.

The results above given clearly show that solutions of compounds of the less electropositive metallic elements with strongly electropositive

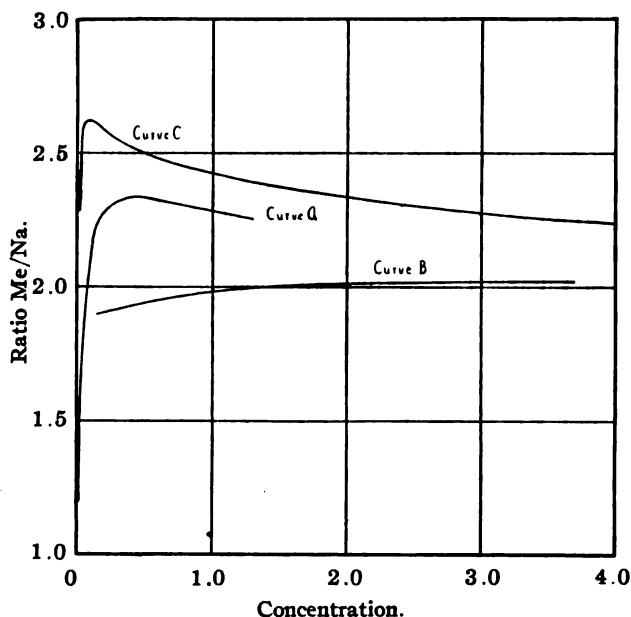


Fig. 1.—The change in the compositions of solutions due to complex formation.

metallic elements are electrolytes, the more electronegative element forming an anion, the number of charges on which corresponds with its position in the periodic system. In the presence of excess of the less electropositive metal, the normal anion reacts with the free metal to form complex anions. The property of tellurium, selenium, antimony, bismuth, lead and tin to form complex anions indicates that this property is in all likelihood a general property of metallic, as well as of non-metallic elements. Indeed, if anything, this property is more pronounced in the more metallic elements than it is in the less metallic elements. That the solutions of the compounds in question are electrolytic may be accepted as an established fact. If the solutions of these substances are electrolytic, then it seems possible, and indeed probable, that the compounds themselves in a free state are salt-like in character; that is, the more

electropositive element is present as cation and the more electronegative element as a more or less complex anion. In what manner the metallic properties of these substances are related to their constitution still remains uncertain. In the case of the tellurium compounds, however, the conclusion seems inescapable that the metallic properties are due to the excess of tellurium atoms in the complex anion, for the normal telluride itself is non-metallic while the complex tellurides are metallic. It should be borne in mind that, while the negative electrons are firmly attached to the electronegative constituent at low concentrations, some of these electrons may readily become movable at high concentrations, for the pure element itself is metallic. At sufficiently high concentrations of the metal or in the pure state, various interactions arise between the charges present in the molecular complex, as a result of which the negative electrons, in part at least, acquire freedom of motion.

#### V. Reaction of Metallic Compounds in Liquid Ammonia Solution

The behavior of solutions of metallic compounds in liquid ammonia clearly indicates that these substances are true electrolytes. They exist in solution in equilibrium with other electrolytes as do ordinary salts and they react with other electrolytes in a similar manner. They undergo metathetical reactions the course of which is determined by the solubility of the compounds formed. With ordinary salts they form metallic compounds which are precipitated from solution when these are insoluble, while they remain in solution when soluble. Thus the lead compound reacts with a cadmium salt according to the equation,  $\text{Na}_2\text{Pb} + \text{Cd}(\text{NO}_3)_2 = 2\text{NaNO}_3 + \text{CdPb}_x$ , the compound  $\text{CdPb}_x$  being precipitated. Whether this compound will remain as such after precipitation depends upon its stability and on other factors. This point has not, as yet, been fully cleared up. On the other hand, with metallic calcium, a reaction takes place according to the reaction equation,  $\text{K}_2\text{Pb}_x + \text{Ca} = \text{CaPb}_x + 2\text{K}$ . Here calcium plumbide is precipitated while metallic potassium remains in solution.<sup>11</sup> With an ammonium salt the following reaction occurs:  $\text{NaPb}_x + \text{NH}_4\text{I} = \text{NaI} + \text{NH}_4\text{Pb}_x$ . The resulting plumbide, however, is unstable, as might be expected, and decomposition occurs at once on precipitation with the formation of ammonia and the evolution of hydrogen, while pure lead is left behind.

Very interesting is the case in which an electronegative ion of a metal is precipitated by means of an electropositive ion of the same metal. For example, sodium plumbide, on the addition of lead nitrate, precipitates lead according to the equation,  $\text{Na}_4\text{Pb}_9 + 2\text{Pb}(\text{NO}_3)_2 = \text{Pb}_2\text{Pb}_9 + 4\text{NaNO}_3$ . The precipitated lead may here be looked upon as a lead plumbide. Whether or not the various lead atoms in the resulting precipitate are equivalent to one another or whether they differ remains

undetermined. It is conceivable that, in the case of metals which are fairly electropositive and which, at the same time, exhibit a pronounced electronegative valence, the metal in the pure state may exist in the form of a compound, a portion of the atoms being positively charged and another negatively charged. Many facts are in harmony with such an hypothesis. It is well known that the more electronegative elements, such as selenium,<sup>16</sup> tellurium,<sup>17</sup> arsenic<sup>18</sup> and antimony,<sup>17,18</sup> are complex in the vapor state. It is not unreasonable to assume that in these complexes some of the atoms function electropositively and others electronegatively. Furthermore, if these elements are complex in the vapor state, then there is all the more reason for believing that they are likewise complex in the liquid state and, indeed, in this state their complexity may be expected to be relatively high. It is well known that sulfur in the liquid state is complex and certain facts indicate that selenium and tellurium in the solid state are complex. Naturally, the complexity of vapors varies as a function of the temperature, the more complex molecules breaking down at higher temperatures. It appears probable that in these complexes the various atoms are not identically involved.

This hypothesis is in harmony with many facts relating to liquid and solid metals. If the values of the equivalent conductance of various metallic elements are compared at ordinary temperatures, it will be found that the strongly electropositive elements are the best conductors, while the more electronegative metallic elements are relatively very poor conductors. The question arises: to what is the difference in the conductance of the various elements to be ascribed? Is it due entirely to a difference in the resistance which the electrons experience in their motion, or is it in part due to the fact that a smaller number of electrons are available in a given volume? If compounds are formed between different atoms of a given element, some of which are charged positively and others negatively, then we should expect that those elements which exhibit the greatest tendency to form compounds of this type would exhibit the lowest equivalent conductance. In the following table are given values of the equivalent conductances of various metallic elements.

TABLE I  
EQUIVALENT CONDUCTANCES OF SOME METALLIC ELEMENTS

Metal	Eq. Cond. $\times 10^6$	Metal	Eq. Cond. $\times 10^6$
Silver.....	6.999	Zinc.....	0.856
Potassium.....	6.503	Indium.....	0.635
Sodium.....	5.288	Strontium.....	0.360
Rubidium.....	4.845	Thallium.....	0.326
Copper.....	4.559	Tin.....	0.313

<sup>16</sup> Brockmüller, *Z. physik. Chem.*, **81**, 129 (1912).

<sup>17</sup> Dobbie and Fox, *Proc. Roy. Soc.*, **98A**, 149 (1921).

<sup>18</sup> Biltz and V. Meyer, *Z. physik. Chem.*, **4**, 263 (1889).

Gold.....	4.547	Lead.....	0.2305
Cesium.....	3.898	Antimony.....	0.1553
Magnesium.....	1.607	Arsenic.....	0.1245
Lithium.....	1.534	Mercury.....	0.0782 (liquid)
Aluminum.....	1.278	Gallium.....	0.0736
Calcium.....	1.228	Bismuth.....	0.0657
Cadmium.....	0.937		

It will be observed that the metals of the first group and the metals of the alkaline earths possess the highest conducting power. As the positive valence of the element increases, its equivalent conductance in general decreases. Such elements as lead, tin, bismuth, antimony, arsenic and tellurium, which exhibit a great tendency to form complex anions, likewise exhibit a low value of the equivalent conductance. May we not conclude, therefore, that the less electropositive metallic elements are not homogeneous; that is, that the various atoms in these elements do not find themselves in the same condition in the liquid and possibly in the solid state.

## VI. The Nature of Metallic Compounds of the Salt Type

Having shown that various metallic compounds dissolved in liquid ammonia are salt-like in character, we may extend the results obtained to compounds which are not soluble in this solvent. So far as the properties of these compounds are concerned, there is nothing to indicate that they differ materially from other compounds whose properties in solution have been studied. For example, there is nothing to indicate that the compounds of sodium with mercury differ materially from those of sodium with tin or lead.

One of the most remarkable facts in connection with intermetallic compounds is the multiplicity of compounds derivable from a given pair of metallic elements. This difficulty, which appears as an insurmountable obstacle to the extension of our valence conceptions to intermetallic compounds, is at once resolved when we take into account the great tendency of metallic elements to form complexes. The existence of complex metallic anions has been conclusively shown as a consequence of the results obtained in the study of solutions of metallic compounds in liquid ammonia. Whether complex cations may likewise exist is, at the present time, uncertain. It is possible, however, that such is the case. Furthermore, the data relative to the composition of metallic compounds are based largely on the properties of metals in the solid state; that is, on the melting-point diagrams. Compounds may appear in a solid state which have a relatively low stability in the liquid mixture; in other words, even very weak forces may lead to the formation of compounds in the solid state. So, for example, sodium and potassium form a compound NaK. Unquestionably this compound has a relatively low stability. At low concentrations such a compound might be expected to be completely dis-



sociated, in all likelihood, into atoms of sodium and of potassium. Dissolved in liquid ammonia, mixtures of sodium and potassium give no indications whatsoever of the existence of a compound.<sup>19</sup> It is probable that many of the compounds in which it would otherwise be necessary to assume a complex electropositive constituent are of this type; that is, they are relatively unstable complexes which are largely restricted to the solid state.

The physical properties of metallic compounds are in harmony with the theory of their constitution, as here outlined. The conductance of metallic compounds in the solid state is almost invariably lower than that of one of the constituents and is often lower than that of both constituents. This is the more true the more electropositive one constituent and the more electronegative the other. It may be inferred that the low conductance of intermetallic compounds of this type is due to the fact that many of the electrons are more or less bound up in the structure of the compound. The more electronegative elements in these compounds presumably bind, more or less firmly, a portion of the electrons available in such systems. In Table II are given values of the specific conductance of a number of metallic compounds. Following the formula of the compound at the head of each column, the values of the specific conductance multiplied by  $10^{-4}$  are given in order for the first element appearing in the formula of the compound, for the compound itself, and finally for the second element in the formula.

TABLE II  
SPECIFIC CONDUCTANCE OF METALLIC COMPOUNDS

Compound	Mg <sub>2</sub> Sn	MgCu <sub>2</sub>	Mg <sub>2</sub> Cu	MgZn <sub>2</sub>	Mg <sub>2</sub> Bi <sub>2</sub>	MgAl	Mg <sub>2</sub> Al <sub>2</sub>
	23.0	23.0	23.0	23.0	23.0	23.0	23.0
$\mu \times 10^{-4}$ .....	0.092	19.4	8.38	6.3	0.76	2.63	4.53
	8.60	64.1	64.1	17.4	0.84	35.1	35.1
Compound	MnAl <sub>2</sub>	FeAl <sub>2</sub>	NiAl <sub>2</sub>	Ag <sub>2</sub> Al <sub>2</sub>	Ag <sub>2</sub> Al	AgMg	AgMg <sub>2</sub>
	22.7	11.0	8.51	68.1	68.1	68.1	68.1
$\mu \times 10^{-4}$ .....	0.20	0.71	3.47	3.85	2.75	20.52	6.16
	35.1	35.1	35.1	35.1	35.1	23.0	23.0
Compound	Ag <sub>2</sub> Sb	Te <sub>2</sub> Sb <sub>2</sub>	TeSn	Te <sub>2</sub> Bi <sub>2</sub>	Cu <sub>2</sub> As		
	68.1	0.017	0.017	0.017	64.1		
$\mu \times 10^{-4}$ .....	0.93	0.48	0.97	0.045	1.70		
	2.56	2.56	8.60	0.84	2.85		

The low values of the conductance of magnesium stannide, Mg<sub>2</sub>Sn, and of the compounds of aluminum are particularly striking. Unless we assume that some of the electrons are bound within the structure of these compounds, it is difficult to account for the low value of the conductance of these substances.

<sup>19</sup> Kraus, *THIS JOURNAL*, 43, 756 (1921).

In the case of compounds in which the more electronegative constituent is non-metallic in the elementary state, the conductance is often very low. In Table III are given values of the specific conductance of a number of compounds of this type. As may be seen from this table, the specific conductance of some compounds is very low while that of others is as high as that of some of the metallic elements.

TABLE III

SPECIFIC CONDUCTANCE OF METALLIC COMPOUNDS<sup>20</sup>

Compound	CuS	PbO <sub>2</sub>	CdO	PbS	Fe <sub>3</sub> O <sub>3</sub> <sup>a</sup>	Fe <sub>3</sub> O <sub>4</sub> <sup>b</sup>
$\mu \times 10^{-4}$ .....	0.85	0.43	0.083	0.042	2.3	0.0116
Compound	FeS <sub>2</sub> <sup>c</sup>		FeS <sub>2</sub> <sup>d</sup>		FeS <sup>e</sup>	Cu <sub>2</sub> O
$\mu \times 10^{-4}$ .....	0.0042		0.060		0.22	0.025

<sup>a</sup>  $\perp$  to axis.    <sup>b</sup> Magnetite.    <sup>c</sup> Pyrite.    <sup>d</sup> Marcasite.    <sup>e</sup>  $\perp$  C-axis.

It is clear that the property of metallicity is not confined to compounds of metals with other metallic elements. There is no substantial reason for believing that metallic oxides and sulfides differ essentially in their constitution from non-metallic oxides and sulfides. Since the latter substances are clearly salt-like in nature, it follows that the metallic condition of a substance does not preclude the possibility of a salt-like structure.

While many metallic compounds are differentiated from the elementary metals in the low value of their specific conductance, in other respects their properties correspond closely with those of elementary metals. For example, the temperature coefficient of the resistance of metallic compounds in the solid state is of the same order of magnitude as that of metallic elements under similar conditions. This would appear to indicate that the conductance change in such compounds is due, in all likelihood, to the increased resistance to motion, which conducting particles experience at higher temperatures, rather than to a decrease in the number of such particles. This statement, however, applies only to metallic compounds in which both constituents are relatively strongly electropositive. In compounds in which one of the constituents is strongly electronegative, the temperature-resistance curve often differs greatly from that for pure metals. In these compounds, at low temperatures, the resistance increases very largely with decreasing temperature, approximately as an exponential function of the temperature. At higher temperatures, the resistance passes through a minimum value, after which it increases more or less normally as a function of the temperature. It may be inferred that in these compounds at lower temperatures a portion of the electrons lose their freedom of motion entirely.

<sup>20</sup> Baedeker, "Die Elektrischen Erscheinungen in Metallischen Leitern," Vieweg, 1911, p. 31.

The mechanical properties of metallic compounds are likewise in agreement with the hypothesis that these compounds are in effect salts. Ductility is one of the characteristic properties of metallic elements. This property is almost entirely lacking in salts, which are invariably hard, brittle substances. Metallic compounds are as a rule hard and brittle.<sup>21</sup> The more electropositive one constituent and the more electronegative the other, the more do metallic compounds resemble salts in their mechanical properties. It is interesting to note that the strongly electronegative metallic elements are relatively hard and brittle in the pure state. This is what might be expected if these elements were compounds between positively and negatively charged atoms or atomic groups of the same element.

The value of the energy changes accompanying the formation of metallic compounds obviously has an important bearing on the theory of their constitution. While anything like complete data is lacking, such data as are available as well as qualitative observations support the view that the reactions involved in the formation of many metallic compounds are similar to those involved in the formation of salts.

TABLE IV  
HEATS OF FORMATION OF METALLIC COMPOUNDS IN KG.CAL.<sup>22</sup>

Compound	CuZn, <sup>23</sup>	MgZn <sub>3</sub>	Mg <sub>2</sub> Al <sub>3</sub>	CuAl <sub>2</sub>	CuZn <sub>10</sub>	CaZn <sub>4</sub>	Cu <sub>2</sub> Cd <sub>3</sub>
Heat per formula wt.	10.14	24.9	164.8	31.9	199.1	55.6	47.7
Compound	MgCd	NaCd <sub>2</sub>	NaCd <sub>4</sub>	NaHg	NaHg <sub>2</sub>	NaHg <sub>4</sub>	KHg <sub>2</sub>
Heat per formula wt.	17.7	30.8	60.6	10.3	17.8	Ca.20	20
Compound	KHg <sub>3</sub>	NaI	Na <sub>2</sub> S	AgI	HgI	HgI <sub>2</sub>	PbS
Heat per formula wt.	Ca.33	69.1	89.3	13.8	14.2	25.2	20.3

In Table IV are given values for the heats of formation of a number of metallic compounds. The energy change accompanying the formation of the compound Mg<sub>2</sub>Al<sub>3</sub> is particularly striking, being approximately 40 Cal. per atom of Mg. This energy change is comparable with that accompanying the formation of many salts, as may be seen from the values given for salts in the table. Corresponding with the high heat of formation of the magnesium-aluminum compound, the electrical conductance of magnesium-aluminum alloys is low. It is well known that strongly electropositive metals combine with the more electronegative metals with great violence. The energy changes accompanying these reactions are certainly greater than those appearing in the above table. In metallic compounds, as in salts, the energy change is the greater the more electropositive one element and the more electronegative the other. For a given

<sup>21</sup> Desch, "Metallography," Longmans, Green and Company, 1910, p. 251.

<sup>22</sup> Roos, *Z. anorg. Chem.*, **94**, 354 (1916).

<sup>23</sup> Herschkowitsch, *Z. physik. Chem.*, **27**, 123 (1898).

electropositive element, the energy change accompanying reaction with another element diminishes as the second constituent becomes less electronegative. There is nothing to indicate that there is a sudden change in the energy effects as we pass from non-metallic to metallic compounds. In salt formation, the accompanying energy effect is largely due to the combination of the negative electron with the electronegative constituent to form an anion. The regularity of the energy effects accompanying the formation of metallic compounds indicates that a similar reaction takes place in the case of these substances. Naturally, the energy changes represent the integrated result of all the forces coming into play when a reaction occurs. Only a broad comparison of the energy relations in salts and metallic compounds has a significance.

### VII. Non-Saltlike Metallic Compounds

While many metallic compounds are of the nature of salts in which the more electropositive constituent is associated with a cation and the more electronegative constituent with an anion, there remains another class of compound metals, often containing non-metallic elements, which resemble the metallic elements in that the negative electrons are not associated with the electronegative elements present. Compounds of this type are sharply differentiated from compounds in which the negative electron is associated with an electronegative constituent, which compounds thus resemble the salts rather than the elementary metals.

The metallic properties of metallic elements are due to the negative electrons in the outer shell of the atom. Any atom which thus contains a negative electron not strongly united to its nucleus is metallic in the free state. In the presence of more strongly electronegative elements, these electrons unite with the electronegative atoms to form a stable complex, *i. e.*, an anion. The atom from which the electron is originally derived is thus electropositive, since it functions as a positively charged complex in the presence of electronegative elements. In the free state, the electropositive complex persists, the negative electrons in the body of the metal not being definitely joined to the atoms.

Many groups of elements exhibit decided electropositive properties in their compounds, and this is true not only of groups containing metallic elements but also of groups containing only non-metallic elements.

The attachment of an electron to the atomic nucleus in the case of non-metallic elements is greatly influenced by the presence of other atoms with which the first atom is combined. The presence of certain atomic groups tends to free the connection between the original atom and its associated electrons. In certain cases, a negative electron is in this manner freed from association with its atom and the resulting compound acquires metallic properties. The property of metallicity is, therefore, not an atomic

property in the sense that it is restricted to metallic elements and their compounds. The negative electron is the constituent to which metals owe their metallic properties and the rôle of the positive constituent is a secondary one.

It is well known that many groups of elements containing either non-metallic elements alone, or both metallic and non-metallic elements, function as stable electropositive ions in their compounds with electro-negative elements. The ammonium group and certain metal-organic groups are familiar examples of this type of positive ions. We should expect that if these groups could be obtained in the free state, the resulting compound would be metallic. Since these compounds contain electro-negative elements, it follows that such groups may prove to be unstable in the free state, for in the presence of negative electrons these elements tend to combine with them with the formation of new compounds. In case the group were stable, however, we should expect it to exhibit metallic properties.

This theory of the constitution of the electropositive groups is borne out by numerous observations. Thus, the ammonium group itself possesses sufficient stability to form an unstable amalgam. The properties of ammonium amalgams clearly indicate a measurable stability of the ammonium group.<sup>24</sup> The substituted ammonium groups, such as tetramethylammonium, possess a much greater stability than the ammonium group. These groups form relatively stable solid metallic compounds with mercury.<sup>25</sup> Even more remarkable are the properties of the tetra substituted ammonium groups in liquid ammonia solutions.<sup>26</sup> These groups may be reduced by electrolysis in ammonia solution. Under these conditions the groups dissolve in ammonia forming a characteristic blue solution which appears in every way identical with solutions of the alkali metals in the same solvent. That such groups are, in fact, typical metals is not to be doubted. Unfortunately, these groups are not sufficiently stable to permit of their being isolated. It is, however, apparent, from their properties in ammonia solution and in their compounds with mercury, that such groups, containing only non-metallic elements, are true metals resembling the alkali metals very closely.

Many metals form electropositive groups with organic radicals of the type  $R_{n-1}M^{n+}$ , where  $n$  is the normal valence of the element and  $R$  is an organic alkyl or aryl group. Compounds of the type  $R_{n-1}M^+X$ , where  $X$  is an anion, exhibit salt-like properties. In general, the smaller the value of  $n$ , the more salt-like is the resulting compound. Mercury salts of the type  $RHgX$  are exceptionally stable and by the electrolysis

<sup>24</sup> Coehn, *Z. anorg. Chem.*, **25**, 430 (1901).

<sup>25</sup> McCoy and Moore, *THIS JOURNAL*, **33**, 273 (1911).

<sup>26</sup> Palmaer, *Z. Elektrochem.*, **8**, 729 (1902). Kraus, *THIS JOURNAL*, **35**, 1732 (1913).

of these salts the free groups  $\text{RHg}$  have been obtained.<sup>27</sup> These groups in the free state are true metals. Even the group  $\text{C}_3\text{H}_7\text{Hg}$ , containing an enormous preponderance of non-metallic atoms, is a true metallic substance. These compounds are, therefore, to be classed with the metallic elements, since the negative electron is not associated with the less metallic elements present.

These free groups throw light on the question as to the source of the negative electrons to which metallic substances owe their metallic properties. The electrons concerned in metallic substances are the valence electrons, that is, the electrons to which chemical reactions are due.<sup>28</sup> Chemical reactions of this type consist essentially in a combination of the negative electron with an electronegative element or group of elements. If the source of electrons is a strongly electropositive element or group of elements and the electronegative constituent is strongly electronegative, then the resulting compound will be an electrolyte, *i. e.*, a salt. Non-salt-like substances are formed only when the negative electron remains associated with both the more electropositive and the more electronegative constituent. All the more electropositive elements thus form salts with strongly electronegative constituents. In salts of elements of high electropositive valence, however, the salt-like characteristics are greatly reduced, as for example, in stannic chloride.

On the other hand, it is not the non-metallic elements alone which possess the power of combining with negative electrons to form stable anions. This property is common to all but the most strongly electropositive metals. The resulting compounds, however, will exhibit metallic properties in the pure state in the case of the less electronegative elements, as a result of interaction between the charges at high concentrations.

Not all compounds, however, are to be ascribed primarily to the interaction of negative electrons. Other forces apparently come into play as a result of which combination occurs. The formation of complex anions is an example of this type. So little is known regarding these substances that it is not possible to venture a guess as to the nature of the mechanism involved in this type of combination.

Another class of metallic compounds in which the negative electron is not primarily concerned is found in the ammoniates of the metals of the alkaline earths. Here we have compounds of the type  $\text{Ca}(\text{NH}_3)_6$ .<sup>29</sup> These compounds appear to be metals whose properties closely resemble those of concentrated solutions of these metals in liquid ammonia. The fact that these compounds are metallic clearly indicates that the negative electrons are not primarily concerned in their constitution. It appears,

<sup>27</sup> Kraus, Ref. 26.

<sup>28</sup> Kraus, Ref. 26, p. 1741.

<sup>29</sup> Kraus, *THIS JOURNAL*, 30, 653 (1908). Biltz, *Z. anorg. Chem.*, 114, 241 (1920).

rather, that the group  $\text{Ca}(\text{NH}_3)_6^{++}$  is a strongly electropositive group of which  $\text{Ca}(\text{NH}_3)_6\text{Cl}_2$  is a salt. An important fact to be noted in this connection is that in the free group the ammonia molecules are similarly combined, *i. e.*, the group breaks down as a whole and not in stages when ammonia is withdrawn. The nature of the mechanism involved in the ammoniated metals, as in the ammoniated salts, remains to be disclosed.

### VIII. Summary

1. It is pointed out that the constitution of substances cannot be derived from their properties in a condensed state with any considerable degree of certainty. In order to determine the constitutions of metallic substances it is necessary to study their properties at low concentrations.

2. At low concentrations the elementary metals are salt-like substances, and it is suggested that metallic compounds will exhibit salt-like properties in even a more decided manner.

3. In solutions of metallic compounds in liquid ammonia, the more electronegative element functions as anion, as follows from the fact that it is precipitated on the anode on electrolysis. *All but the strongly electropositive elements exhibit a negative as well as a positive valence.*

4. The normal anions of metallic elements form complex anions in the presence of the element in question. These complex metallic compounds are similar to the complex iodides and sulfides which have been studied in aqueous solution. *The property of forming complex anions is one common to many metallic as well as non-metallic elements.*

5. It has been shown that the complex telluride ion carries two charges. In solution in ammonia the complex anions  $\text{TeTe}^{--}$  and  $\text{Te}_3\text{Te}^{--}$  exist. It may be inferred that the anions of the metals of the fifth group carry 3 and those of the fourth group 4 charges.

6. Since it has been shown that the metals selenium, tellurium, bismuth, antimony, arsenic, lead and tin form complex anions in ammonia solution, it may be inferred that other metals not soluble in ammonia form similar complex anions. *Metallic compounds of this class are, therefore, virtually salts.*

7. The multiplicity of compounds derivable from a given pair of metallic elements is accounted for on the hypothesis that in their compounds the more electronegative elements form complex anions. This brings metallic compounds into line with present conceptions of atomic structure.

8. The physical properties of metallic compounds are in harmony with the hypothesis that they possess a salt-like structure.

9. It is pointed out that the energy effect accompanying the formation of metallic compounds is of the same order of magnitude as that accompanying the formation of salts. As in the case of salts, the energy change

is the greater the more electronegative one element is with respect to the other.

10. Electropositive groups, such as the ammonium group, are virtually metals although their stability in the free state is not sufficient to permit their isolation in most instances. The most stable groups possess sufficient stability to demonstrate their metallic properties in the free state. Such groups resemble elements in their properties.

11. *The property of metallicity is not an atomic one.* It may be imparted to non-metallic elements by combination with other non-metallic elements. *The metallic state is due to the presence of uncombined negative electrons.*

12. The electrons which impart metallic properties to an element are those to which the chemical reactions of this element with other elements are due.

13. The reaction between strongly electropositive and strongly electronegative elements or groups of elements consists essentially in a combination of the negative electrons of the electropositive constituent with the atoms of the electronegative constituent.

14. In the metal ammoniates of the type  $\text{Ca}(\text{NH}_3)_6$ , which are metallic substances, the negative electrons are not primarily concerned.

The detailed experimental material on which this paper is based will appear in forthcoming publications. The experimental work has been in part supported by grants from the Warren Fund of the American Academy of Arts and Sciences. I wish to acknowledge my indebtedness to these grants which have greatly facilitated the accumulation of the necessary experimental material.

WORCESTER, MASSACHUSETTS

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[CONTRIBUTION FROM THE GATES CHEMICAL LABORATORY OF THE CALIFORNIA INSTITUTE OF TECHNOLOGY, No. 12]

## THE CRYSTAL STRUCTURES OF THE HEXAMMONIATES OF THE NICKEL HALIDES

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**Introduction.**—When an excess of ammonium hydroxide is added to a solution of one of the nickel halides, small octahedral crystals are precipitated. These crystals have the composition  $\text{NiX}_2 \cdot 6\text{NH}_3$ , where X is chlorine, bromine or iodine.

Single crystals of considerable size can be grown by slow cooling from a not too strong solution. These are rarely perfect in internal structure and all of them are extremely fragile. Because of the ease with which

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they shattered, thin sections could not be prepared and the X-ray observations had to be carried out upon entire crystals.

Microscopic examination showed these crystals to be completely isotropic. Nothing is known, however, concerning the class of the cubic system to which they should be assigned. Goniometric observations would be possible only at a low temperature, because owing to decomposition through loss of ammonia the crystal faces tarnish almost immediately after removal from the solution. The preparation of Laue photographs, which required several hours, was accomplished by imbedding the specimen in wax, thus inhibiting this decomposition.

This study of crystal structure was carried out by the aid of the generally applicable methods based upon the use of the theory of space groups which have already been described.<sup>2</sup>

**The Unit Cell and the Number of Associated Molecules.**—Comparison reflection photographs against a cleavage face of calcite and an octahedral face of a crystal of  $\text{NiCl}_2 \cdot 6\text{NH}_3$  were prepared in the usual manner.<sup>3</sup> Values of  $d_{\text{III}}/n$  (the ratio of the spacing of octahedral planes into the order of the spectrum) obtained from this photograph combined with the density (1.526) as determined by a flotation and a determination of the density of the floating liquid by a Westphal balance gave the value 0.509 for the ratio  $m/n^3$ , in which  $m$  represents the number of molecules in the unit of structure and  $n$  the order of the spectrum. From an examination of a table<sup>4</sup> of possible values of  $m/n^3$  it is evident that either  $m = 4$  with  $n = 2$  or else that  $m = 32$  with  $n = 4$ . Measurements upon reflection photographs of the corresponding bromide and iodide showed that they likewise have either 4 or 32 chemical molecules within the unit cell.

**The Structure of  $\text{NiCl}_2 \cdot 6\text{NH}_3$ .**—If it is assumed that  $n$  is 4, the mean value of the length of the side of the unit cube is found to be 10.09 Å. U. (or  $10.09 \times 10^{-8}$  cm.).

The observation (made on the Laue photographs) that only planes all of whose indices are odd reflect in the first order shows that, if 4 molecules are contained in the unit cell, this crystal must have the symmetry of one of the space groups  $T_h^3$ ,  $O^3$  or  $O_h^5$ . Neglecting the positions of the hydrogen atoms, which contain so few electrons that they cannot be located, all of the arrangements for this salt arising from these three space groups are identical.<sup>5</sup> It will, moreover, be observed that, neglecting the

<sup>2</sup> Wyckoff, *Am. J. Sci.*, 50, 317 (1920). Wyckoff and Posnjak, *THIS JOURNAL*, 43, 2292 (1921); etc.

<sup>3</sup> Wyckoff, *THIS JOURNAL*, 42, 1100 (1920).

<sup>4</sup> Wyckoff, *Am. J. Sci.*, 1, 138 (1920).

<sup>5</sup> All the space-group arguments of this paper are based upon a series of tables which form part of a book entitled "An Analytical Expression of the Theory of Space Groups" which is shortly to be published by the Carnegie Institution of Washington.

hydrogen atoms in both cases, the problem of the positions of the atoms in ammonium chloroplatinate already discussed in a previous article<sup>6</sup> (if it be considered that chlorine atoms replace nitrogen atoms, nickel atoms replace the platinum atoms, and the nitrogen atoms of ammonia replace the chlorine atoms) is identical with the present one. In the first order region some planes with greater spacing are much more intense than those with lesser (see Table I), and hence the arrangement of the nitrogen atoms about the nickel atoms must be the same as the grouping of the chlorine atoms about the platinum atoms of ammonium chloroplatinate. The two salts are thus (except for the positions of the hydrogen atoms) completely isomorphous, and a detailed treatment of the present case is unnecessary.

An approximate determination of the position of the nitrogen atoms within the unit cell can be obtained from a study of the relative intensities of reflections from planes appearing in the first order. The calculated wave lengths and estimated intensities of relevant reflections obtained in Laue photographs are given in Table I. The customary intensity equations (strictly analogous to those prevailing in the case of ammonium chloroplatinate) have the following form for first order reflections from planes having all odd indices.

$$A = 4\bar{N}i + 8\bar{N}(\cos 2\pi hu + \cos 2\pi kv + \cos 2\pi lw)$$

By plotting the amplitudes (or intensities) calculated by this expression for each of the planes of Table I over a range of values of  $u$  and comparing the calculated and observed relative intensities of planes having approximately the same spacings, the value of  $u$  can be located within fairly narrow limits. The presence of a strong fourth order and the absence of a third order reflection from the (111) face show that  $u$  is either near 0.25 or 0.50. The region around 0.50 can be eliminated from a consideration of first order reflections. The data recorded in Table I show that  $u$  must have a value less than 0.25 and lying probably between the limits 0.227 and 0.245. This lower limit is set by the observation that the plane  $11\bar{5}3$  reflects less strongly than the more complicated plane  $9\bar{7}7$ . If the scattering powers of nitrogen and nickel were proportional to their atomic numbers (which probably is only very roughly true) the appearance of such planes as those of the forms  $377$  and  $11\bar{7}7$  would locate the lower limit in the neighborhood of 0.24. The absence of marked discrepancies amongst the second order reflections from planes having even indices is in agreement with this value for  $u$ .

The coördinate positions of the atoms of  $NiCl_2 \cdot 6NH_3$  within the unit cube are thus as follows:<sup>6</sup> Nickel, arrangement 4(b); Chlorine, arrangement 8(c); Nitrogen, arrangement 24(a).

The placing of the hydrogen atoms presents some ambiguity. Since

<sup>6</sup> Wyckoff and Posnjak, Ref. 2.

there are not 72 equivalent positions within the unit cell of any cubic crystal, it is evident that the 3 hydrogen atoms in the ammonia group cannot be equivalent to one another. Inspection of the possible space groups shows that 48 of these atoms must be alike, and different from the other 24; that is, two of the hydrogen atoms of the ammonia in this compound are different from the third. The special cases having 48 equivalent positions in the unit are different for the space groups belonging to different classes of cubic symmetry. If the correct class for this crystal were known, it would be possible to determine therefrom the manner of arrangement of the hydrogen atoms about the nitrogen atom. It can readily be shown that, were the symmetry of this crystal holohedral, or enantiomorphically hemihedral, the two like hydrogen atoms would

TABLE I  
LAUE PHOTOGRAPHIC DATA FOR  $\text{NiCl}_2 \cdot 6\text{NH}_3$

First photograph				Second photograph*			
Form of reflecting plane	Relative spacing	Wave length	Estimated intensity	Form of reflecting plane	Relative spacing	Wave length	Estimated intensity
351	0.169	0.480	10	133	0.229	0.465	8
335	0.152	0.425	9	135	0.169	0.464	10
155	0.140	0.390	10	355	0.130	0.315	8
137	0.130	0.479	3—	337	0.130	0.358	2
355	0.130	0.473	8+	157	0.115	0.464	7
373	0.122	0.305	0.3	357	0.109	0.453	3
751	0.115	0.409	2	139	0.105	0.338	3
557	0.100	0.458	3	177	0.100	0.408	1
195	0.096	0.446	2	159	0.096	0.277	2
195	0.096	0.455	2+	159	0.096	0.293	2
377	0.096	0.440	0.2	159	0.096	0.415	5
577	0.090	0.396	0.2	359	0.093	0.277	1
197	0.087	0.377	0.5	577	0.093	0.301	1
379	0.085	0.479	0.2	1 3 11	0.087	0.373	1
1 5 11	0.082	0.483	0.2	179	0.087	0.305	1
579	0.080	0.475	0.3	559	0.087	0.365	2
599	0.073	0.378	0.1	379	0.085	0.346	2
...	...	...	..	1 5 11	0.082	0.462	2+
...	...	...	..	3 5 11	0.080	0.479	1
...	...	...	..	579	0.080	0.476	2
...	...	...	..	779	0.075	0.480	2

\* Reflections, but of intensities too weak for satisfactory comparisons, have been observed from planes of the following forms: 199, 1 7 11, 1 3 13, 1 5 13, 3 5 13, 3 9 11, 7 7 11, 1 1 15, 5 9 11, 1 3 15, 9 9 11, 9 11 11. These recorded estimates of intensity are necessarily very inexact. Especially in the data from this second photograph no quantitative significance should be attached to intensities of unity or less.

be equally shared by neighboring nitrogen atoms; consequently an ammonia group would not exist within such a crystal. This is so contrary to what would have been expected from chemical considerations that in the absence of any satisfactory crystallographic determination of its class of

symmetry, it is more natural to assign this salt to the space-group  $T_h^3$  with paramorphic (pyritohedral) hemihedry. The positions of the hydrogen atoms thus probably become

Hydrogen: 24 atoms at  $\infty 00$  and the other positions of special case 24(a); 48 atoms at  $0u'v'$  and the other positions<sup>7</sup> of special case 48(b).

The relative positions within the unit cell of the atoms of  $NiCl_2 \cdot 6NH_3$  are readily seen with the aid of Fig. 7 in the previous article on the structure of ammonium chloroplatinate by remembering that in that figure the positions of the hydrogen atoms must be omitted from consideration, that nickel atoms replace platinum atoms, and that nitrogen and chlorine atoms are interchanged.

In common with practically all crystal structure determinations, it is at present impossible to eliminate uniquely all of the more complicated structures which could be developed for  $NiCl_2 \cdot 6NH_3$ . The simple structure having 4 molecules within the unit cell is nevertheless in such complete accord with the experimental data that there can be no doubt of its essential correctness. It would be possible to develop an arrangement having 32 molecules within the unit which would approach so very close to the simple structure as to be indistinguishable from it by any means now available. There is no reason for considering seriously such a complicated structure, and its assumption would not relieve this determination of the arrangement of the atoms of  $NiCl_2 \cdot 6NH_3$  of any of its chemical implications.

**The Structure of  $NiBr_2 \cdot 6NH_3$ .**—This salt is completely analogous in its structure to the chloride. The length of the side of the unit cell having 4 molecules within it was determined to be 10.48 Å. U. An attempt was not made to effect an accurate placing of the nitrogen atoms.

**The Structure of  $NiI_2 \cdot 6NH_3$ .**—The arrangement of the atoms in this crystal is the same as that prevailing in the chloride. When  $m = 4$  the length of the side of the unit cube was found to be 11.01 Å. U.

Three Laue photographs were completely analyzed in the endeavor to accumulate sufficient data to place the nitrogen atoms with accuracy. Because of the slightly imperfect character of the crystals employed and especially because of the much greater absorption of this salt, first order reflections from only a few planes with complicated indices could be attained. Some useful data from these photographs are recorded in Table II. From the plots of the amplitude against the parameter  $u$  for these planes (which are the same as those of the chloride) it is evident that  $u$  in this case also has a value somewhat under 0.25, but greater than 0.20. If the scattering powers of different elements were proportional to their atomic numbers, then the value of  $u$  could hardly be much less than 0.24.

<sup>7</sup> The values of these coordinate positions will be given in "An Analytical Representation of the Theory of Space Groups" to which reference has already been made.

A further indication of the value of  $\mu$  is furnished by a comparison of the intensities of reflection in the second order region of planes containing even indices. Thus the two planes 035 and 343, both of which have the same relative spacing (0.171), reflect wave lengths of 0.780 Å. U. and 0.778 Å. U. with estimated intensities of 3.1 and 3.0. In the region between 0.20 and 0.25 this practical equality of reflecting powers could only be found if  $\mu$  has a value not much less than 0.24.

**The Significance of these Structures.**—According to this determination of structure all 6 of the ammonia molecules of  $\text{NiX}_2 \cdot 6\text{NH}_3$  must be alike and related in the same manner to a central nickel atom to which they approach more closely than to any other atom of the compound. It seems therefore entirely appropriate to write the formula of these compounds in the customary coördination manner,  $\text{Ni}[6\text{NH}_3]\text{X}_2$ .

TABLE II  
LAUE PHOTOGRAPHIC DATA FOR  $\text{NiI}_2 \cdot 6\text{NH}_3$

First photograph				Second photograph			
Form of reflecting plane	Relative spacing	Wave length	Estimated intensity	Form of reflecting plane	Relative spacing	Wave length	Estimated intensity
133	0.229	0.446	2	335	0.152	0.415	2
135	0.169	0.432	5	155	0.140	0.400	8
335	0.152	0.488	1	355	0.130	0.488	5
155	0.140	0.450	3	157	0.115	0.490	1
355	0.130	0.467	5	557	0.100	0.460	1
137	0.130	0.467	1	159	0.096	0.468	0.8
157	0.115	0.440	2	...	...	...	...
557	0.100	0.384	0.1	...	...	...	...
159	0.096	0.489	0.3	...	...	...	...
1 5 11	0.082	0.485	0.1	...	...	...	...
1 7 11	0.076	0.481	0.1	...	...	...	...

These hexammoniates have been shown to have identically the same arrangement of their atoms as the grouping which prevails in the chemically rather dissimilar ammonium chloroplatinate. The hexammoniate chloride and potassium chlorostannate, which is isomorphous with ammonium chloroplatinate, have furthermore almost identical distances between their corresponding atoms.<sup>8</sup> In potassium chlorostannate at least 4 of the chlorine atoms would be ordinarily considered to be held to the tin atom by primary valence forces; but the union between the nickel atom and the neutral ammonia molecules is a typical secondary valence bonding. From this observation that ammonia molecules are just as intimately associated with a nickel atom in  $\text{NiCl}_2 \cdot 6\text{NH}_3$  as are the chlorine atoms with a tin atom in potassium chlorostannate, it is difficult to escape from the conclusion that in the crystalline state there need not be differences between the arrangements of atoms held by what chemists have been accustomed to call primary and secondary valence forces.

<sup>8</sup> Dickinson, *THIS JOURNAL*, 44, 276 (1922).

In ammonium chloroplatinate it was shown that the distance between the platinum atom and the chlorine atoms is in close accord with that demanded by the principle of close packing of atoms as stated by W. L. Bragg.<sup>9</sup> The same thing is true of the distance between tin and chlorine in potassium chlorostannate. In neither of these compounds, however, are the distances between any other pairs of atoms in satisfactory agreement with this principle. In these nickel halides, furthermore, contacts between atoms having the radii given by W. L. Bragg seem impossible except between nickel and ammonia. It cannot be determined whether such a contact is established in this direction, because of the uncertainty as to whether the hydrogen atom having the arrangement of 24(a) has a value of  $v$  which is greater or less than 0.24. The distance between the nickel atom and the nitrogen atom in all three halides greatly exceeds the sum of the radii of nickel and nitrogen. It was hoped that the value of  $u$  could be sufficiently accurately determined in  $\text{NiI}_2 \cdot 6\text{NH}_3$  so that the possibility of a close packing between nickel atoms and ammonia groups could be definitely decided. Though this could not be conclusively done, the existing evidence seems to favor for  $u$  nearly the same value in both the chloride and iodide; if this is true, then no close packing of atoms having the radii assigned by W. L. Bragg would be possible within these crystals.

### Summary

It has been shown that in the arrangement of their atoms the hexammoniates of nickel chloride, bromide, and iodide are strictly isomorphous with ammonium chloroplatinate. The dimensions of the unit cells for each of these salts and the values of the variable parameters defining the positions of the nitrogen atoms in the chloride and iodide have been estimated. The chemical significance of this structure within which some of the atoms are bound together by a purely secondary valence is mentioned.

PASADENA, CALIFORNIA

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<sup>9</sup> W. L. Bragg, *Phil. Mag.*, [6] 40, 169 (1920).

[CONTRIBUTION FROM THE CHEMICAL LABORATORY, MARYLAND ACADEMY OF SCIENCES]

## THE ELECTRICAL PRECIPITATION OF COLLOIDS

BY CLAUDE HAINES HALL, JR.

Received February 21, 1922

## Introduction

Bancroft<sup>1</sup> suggests in his list of research problems in colloid chemistry that the precipitating action of high potential current on colloidal suspensions in non-conducting liquid media should be investigated. There is apparently no literature upon this phase of the subject although a great deal of work has been done by Cottrell,<sup>2</sup> Strong,<sup>3</sup> and many others<sup>4,5</sup> on the electrical precipitation of fogs and smokes.

The theory of smoke precipitation has been thoroughly worked out by those mentioned, and is easily available so that it would serve no useful purpose to review it here. The case of the precipitation of sols is somewhat analogous to that of smokes although, of course, the viscosity of the medium is much greater and the electrical resistance of the medium is considerably higher. The optimum condition for the precipitation of smoke is a potential of about  $5 \times 10^4$  volts, direct current, having the point or wire negative.<sup>4</sup> The temperature is not important.<sup>3</sup> On the basis of these data the precipitation of sols was attempted.

## Experimental

The medium used was a very high grade transformer oil.<sup>6</sup> It was rated by the manufacturer and also by a testing laboratory as having a resistance of  $1.5 \times 10^{16}$  ohms per centimeter cube. The suspensions were prepared by several methods, the data for two of those used in the following tests being given as representative.

Test 4.—Two aluminum electrodes, connected to a  $10^4$  volt transformer, were suspended in the oil and arranged so that they could be touched together and then separated a short distance. An arc was thus formed and maintained until the desired density was reached (about 10 minutes).

Test 1.—A sample of the oil was saturated with arsenic iodide<sup>7</sup> and hydrogen sulfide passed in until the arsenic was completely precipitated.

<sup>1</sup> Bancroft, *J. Ind. Eng. Chem.*, **13**, 350 (1921).

<sup>2</sup> Cottrell, *ibid.*, **3**, 352 (1911); *Smithsonian Rpt.*, **1913**, 653.

<sup>3</sup> Strong, *Proc. Am. Inst. Elec. Eng.*, **34**, 387 (1915).

<sup>4</sup> Nesbit, *ibid.*, **34**, 405 (1915).

<sup>5</sup> Bradley, *ibid.*, **34**, 421 (1915).

<sup>6</sup> Supplied through the courtesy of Mr. E. P. Early of the Standard Oil Co.

<sup>7</sup> Unpublished solubility tables.

This method makes a very dense and homogeneous sol, which will remain in suspension almost indefinitely.<sup>8</sup>

A number of forms of precipitation apparatus were tried out but most of them were found unsatisfactory owing to the great tendency of the current to break through. The form finally adopted was a vertical tube of Pyrex glass, 2 cm. in diameter and 35 cm. long, fitted with a circular platinum disk electrode at one end and a sharply pointed adjustable platinum wire at the other.

The coil used to supply the voltage was a  $2 \times 10^5$  volt X-ray coil. For direct current work it was operated on 115 volts in connection with a battery of 3 electrolytic interrupters and a suitable primary condenser. A "point-to-plate" rectifier was inserted in the secondary circuit to suppress any "make" current. The secondary connections were carried directly, suitably suspended, to the electrodes of the tube and a test gap shunted across them. For alternating current tests the same coil was supplied with 80 volts from a small synchronous converter connected to the power lines. The interrupter, condenser and rectifier were, of course, omitted.

TABLE I  
EXPERIMENTAL DATA

No.	Suspension	Nature of charge on point	Secondary potential (Alternate gap in cm.)	Input Kw.	Time Min.
1	As <sub>2</sub> S <sub>3</sub>	- D.C.	28	2	200
2	HgS	- D.C.	20	2	70
3	Fe <sub>4</sub> (FeCy) <sub>3</sub>	- D.C.	20	2	60
4	BaSO <sub>4</sub>	- D.C.	20	2	120
5	Al	- D.C.	28	2	200
6	Cu	- D.C.	20	2	100
7	Pb	- D.C.	20	2	60
8	Ag	- D.C.	20	2	120
9	Fe	- D.C.	20	2	120
10	As <sub>2</sub> S <sub>3</sub>	+ D.C.	28	2	100
11	HgS	+ D.C.	20	2	120
12	Al	+ D.C.	25	2	130
13	Cu	+ D.C.	20	2	70
14	As <sub>2</sub> S <sub>3</sub>	A.C.	16	1.5	200
15	HgS	A.C.	12	1.2	90
16	BaSO <sub>4</sub>	A.C.	14	1.2	150
17	Al	A.C.	10	1	100
18	Pb	A.C.	10	1	60

The results were in every case the same. No matter how long the apparatus was run or what potentials were employed no sign of precipi-

<sup>8</sup> No difficulty was experienced from muddying of the oil when the sol was prepared by chemical methods. With the electrical method it is necessary to keep the current density very low (less than 0.01 ampere at the electrodes) if muddying is to be prevented.



tation was observed.<sup>9</sup> After each test the sol was removed from the precipitation tube and allowed to stand along with a sample of the same sol which had not been treated. No difference in the rate of settling could be noted although suspensions of widely differing coarseness were used, as may be seen from the fact that Test 6 settled in about 24 hours while Test 1 has not settled in over 6 months. The inevitable conclusion is that under the experimental conditions cited it is impossible to precipitate colloidal suspensions in non-conducting, liquid media by electrical means.

### Theoretical

It is of interest to investigate the mathematical grounds for the failure of electrical precipitation in the case of sols. As Strong<sup>3</sup> has shown in connection with smoke, the energy required for the precipitation of a colloid is  $E = n(1/2mV^2 + Fs)$  where  $E$  is the energy in ergs per unit volume,  $n$  the number of particles,  $m$  the average mass of the particles,  $V$  is the transverse velocity imparted to the particles,  $F$  is the frictional resistance, and  $s$  is the average distance traversed.

Stoke's law, which has been found to hold with considerable accuracy, gives  $F = 6\pi\mu adV$ . Also  $m = 4/3\pi da^3$  and  $s = l$ , where  $d$  is the density of the particles,  $a$  the average radius,  $\mu$  the viscosity of the medium, and  $l$  the distance from point to plate for point electrodes, or the radius of the cylinder for cylindrical electrodes. Substituting, the formula becomes  $E = 2/3\pi da^3V^2 + 3\pi\mu adlV$ .

Roughly evaluating the relative constants as

	Smokes	Sols
$\mu$	$2 \cdot 10^{-3}$	1
$a$	$10^{-3}$	$10^{-4}$
$l$	1	1
$d$	$10^{-2}$	1
$V$	$V_f$	$V_s$

transforming the above equation to a comparative form

$$2da^3V_s^2 + 9\mu a_s d_s l_s V_s = 2d_f a_f^3 V_f^2 + 9\mu_f a_f d_f l_f V_f$$

substituting the constants and solving for  $V_s$  in terms of  $V_f$ .

$$V_s = \frac{-10^{-4} \pm \sqrt{10^{-8} + 16 \cdot 10^{-18}(10^{-17}V_f^2 + 10^{-7}V_f)}}{4 \cdot 10^{-18}}$$

and expanding and simplifying (using the positive sign which gives the only root with a physical significance) we obtain,

$$V_s = 2 \cdot 10^3(10^{-7}V_f + 10^{-17}V_f^2) + 10^{-3}(10^{-7}V_f + 10^{-17}V_f^2) + - \\ V_s = 2 \cdot 10^{-4}V_f + - + - - -$$

<sup>9</sup> No corona effect was observed owing possibly to the opacity of the suspension, although the conditions in some of the tests must have been such that it could exist, particularly in Test 14. In Test 1 the electrodes were later drawn slowly together until spark-over occurred, no corona being observed.

That is, that the velocity of precipitation for the same energy, applied to the particle, would be 20,000 times as great for smokes as for sols. This confirms the experimental evidence of the very slow precipitation.

### Summary

The author has investigated the effect of high potentials upon colloidal suspensions in non-conducting liquids. There has been no precipitation detected in the range  $10^4 - 2 \times 10^5$  volts, either alternating or direct current.

It is shown that the rate of precipitation would be  $1/20000$  of that for smoke for the same energy applied to the particle.

The author wishes to acknowledge his gratitude to Mr. William Haggenbotham for the valuable assistance rendered him in the course of the investigation.

BALTIMORE, MARYLAND

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF CLARK UNIVERSITY, No. I, 11]

## THE EQUILIBRIUM IN LIQUID MIXTURES OF AMMONIA AND XYLENE

BY CHARLES A. KRAUS AND EDWARD H. ZEITFUCHS

Received March 8, 1922

### Introduction

Franklin and Kraus have observed that mixtures of ammonia and *meta*-xylene have an upper critical end-point<sup>1</sup> a little below room temperatures. Since the vapor-pressure curves of only a few such systems have been studied thus far,<sup>2</sup> it appeared worth while to investigate this system in some detail. In as much as the vapor pressure of xylene is low compared with that of ammonia, the total-pressure curves will differ little from the partial-pressure curves.

In the present investigation the vapor pressure of various liquid mixtures has been determined together with the composition of the liquid phases of the monovariant system. The latter data were determined in a separate series of experiments.

The critical end-point was determined in a special experiment by direct observation of the temperature at which the two phases become identical. For this purpose ammonia and *meta*xylene were sealed in a heavy walled

<sup>1</sup> This is sometimes called the critical point of solution. Since such a point also occurs in the diphasic system, it appears preferable to designate the critical point of the three-phase system as critical end-point, as has been suggested by Büchner.

<sup>2</sup> The literature relating to systems of this type has been collected by Büchner in Part 2, Vol. II, of Roozeboom's "Die Heterogenen Gleichgewichte vom Standpunkte der Phasenlehre," and detailed references may accordingly be omitted here.

glass tube provided with an electromagnetic stirrer. This tube was placed in a bath, contained in a Dewar tube, the temperature of which was allowed to rise slowly. Keeping the mixture vigorously stirred, the temperature was noted at which the two-phase system disappeared. The mean value so found for the critical end-point was  $14.7^{\circ}$ .

### The Vapor Pressure of Liquid Mixtures of Ammonia and Xylene

**Apparatus.**—The boiling point of the *metaxylene* used in this work was found to be close to  $139.2^{\circ}$ , the value given in Landolt-Börnstein's Tables of Physico-chemical Constants for the boiling point of pure *m*-xylene. The ammonia was drawn from a container in which it had been purified by the method given by Franklin and Kraus.<sup>3</sup> The arrangement of the apparatus used to measure the total pressure of the vapor of mixtures of liquid ammonia and liquid xylene is shown in Fig. 1.

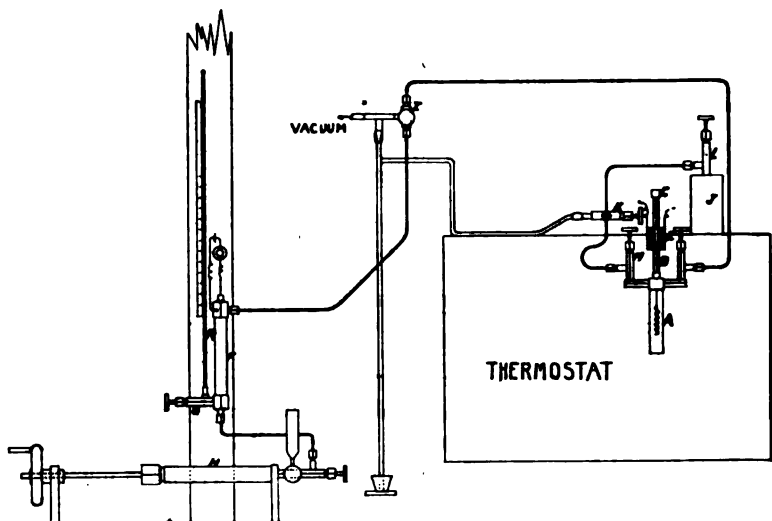


Fig. 1.—The apparatus employed in determining the vapor pressure of the monovariant system.

All parts of the apparatus which were under pressure were constructed of metal, with the exception of the mercury column *R*, which was made of glass tubing of 1 mm. thickness and 4 mm. internal diameter.

The liquid mixture was contained in a thin walled steel tube *A* of 2.75 cm. internal diameter and 15 cm. length. This tube was suspended in a thermostat containing kerosene which was vigorously stirred and whose temperature could readily be controlled within  $0.01^{\circ}$ . The total volume of the liquid mixture in Tube *A* varied from 30 cc. to 70 cc., depending on the composition. A brass tube, *B*, 12 mm. o. d. by 9 mm. i. d., and 20 cm. long, was screwed and soldered to *A*. A steel core, having a diameter of 8 mm. and a length of 7.5 cm. was supported in the bore of the brass tube by a steel piano wire spring of No. 31 B. and S. gage. This spring was fastened to the brass cap *C* which was

<sup>3</sup> Franklin and Kraus, *Am. Chem. J.*, 23, 284 (1900).

screwed into a conical seat on the top of the tube *A*. A plunger stirrer was suspended from the steel core by means of a heavy steel wire. The core was actuated by means of a solenoid *E* in which the current was interrupted once per second by means of a motor driven contact breaker. The degree of stirring could be regulated by adjusting the position of the solenoid along the axis of the brass tube and by resistance placed in the solenoid circuit.

Connection was made with the manometer *R* by means of a mercury reservoir *F* of thin walled steel tubing of 27 mm. i. d. and 17.5 cm. length. To its ends were welded 2 short pieces of hexagonal steel which were machined to take the various connections. Connection with the mercury column was made through the valve *G*. The column had a height of 7.2 meters. A plug carrying an insulated platinum contact point was screwed into the top of *F*. By means of this contact point, which projected into a small opening near the top of the mercury reservoir, the level of the mercury could be maintained at a fixed point with ease and precision. The position of the platinum point was transferred to a point on a steel tape suspended alongside the manometer column. Contact of the mercury with the platinum point was indicated by means of a small electric lamp. The amount of mercury in the reservoir was regulated by means of the mercury displacement piston *H*.

Connection between the tube *A*, containing the liquid ammonia-liquid xylene, and the mercury reservoir *F*, was made by means of a small bore steel tube as shown. This capillary steel tube connection was provided with a valve at *I*, by means of which the space above the mercury in the reservoir and the tube *F* and in the connecting tube could be evacuated.

The ammonia supply was contained in a light steel cylinder *J*. The steel capillary tube connecting this container and the tube *A* could be evacuated at will through the valve *K*. The desired quantity of ammonia was distilled from the container *J* into the tube *A* on opening valves *L* and *M*. During the distillation, the temperature of the thermostat was maintained near 8°, while the ammonia container was slightly warmed by resting it on a small electrically heated plate. The quantity of ammonia, which distilled into *A*, was obtained by difference in the weight of the container before and after the distillation.

The description of the method of determining the total vapor pressure of a mixture of liquid xylene and liquid ammonia by means of this apparatus follows.

**Experimental Method.**—For a mixture of a desired composition, the proper amount of xylene was introduced into *A* through *B* by means of a weight pipet having a long stem. *B* was then closed by Cap *C*, and *A* was evacuated. The desired quantity of ammonia was next distilled into *A* from *J* in the manner described above. The plunger stirring the liquid in *A* was then set in motion and the temperature of the bath was brought to the value desired.

The valve *G* connecting the mercury column and the mercury reservoir was then cautiously opened and the column allowed to adjust itself to the pressure in the apparatus, after which mercury was forced into the reservoir by means of the displacement piston *H* until contact was made with the platinum point. The position of the top of the mercury column was read on a graduated steel tape suspended with its zero point near the top of the column. As soon as the position of the meniscus of the mercury

column became constant, two readings were made at intervals of 10 minutes. The height of the column of mercury was given by the difference in reading of the position of the platinum point and the position of the top of the mercury column. The temperature of the column was obtained from thermometers placed at 120cm. intervals along its height. The barometric height and the temperatures were read for every measurement of the height of the manometer column, and the temperature of the room in the immediate neighborhood of the apparatus was noted. The temperature of the thermostat was then changed to the one next desired and the procedure for measuring the pressure, as just described, was repeated.

In general, for a given composition, the run was started at 8° and measurements of the pressure were made at 8°, 10°, 12°, 14°, 15°, 17° and 20°. In some cases, for a mixture of given composition, the pressure measurements were repeated at the various temperatures as the temperature was varied from 8° to 20° and back from 20° to 8° by the intervals given above. The agreement of the measurements in any such case was found to lie well within the limits of error involved in other parts of the experimental work.

**Experimental Results.**—In Table I are given in detail the data as obtained for a complete run at some one composition. In Table II are

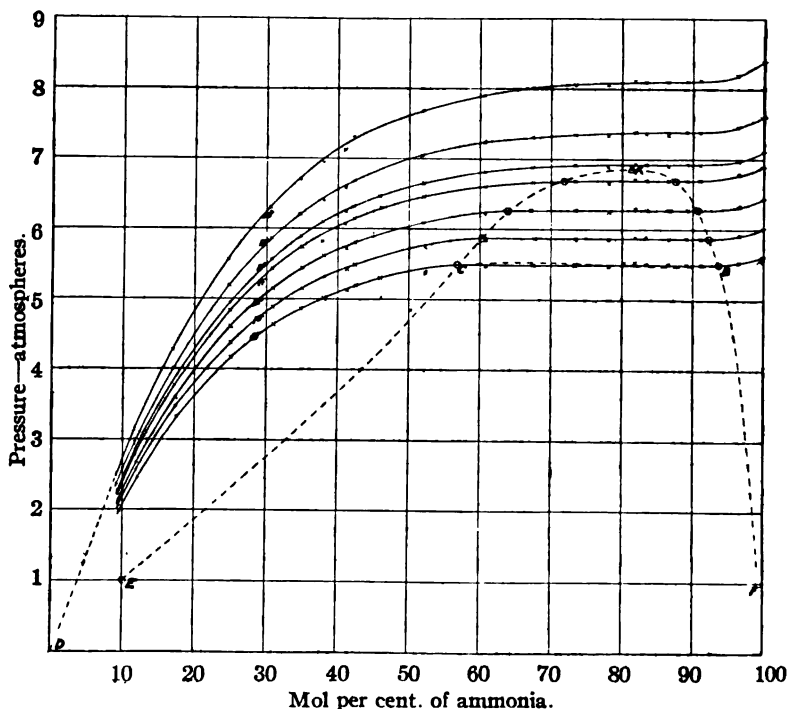


Fig. 2.—Isotherms of the mixtures.

given the values of temperature, pressure, and mean composition for all experiments which were considered satisfactory. It was necessary to correct the total composition of the liquid ammonia-xylene mixtures for the amount of ammonia in the vapor above the liquid in *A* and in the tube connecting this reservoir with *F*. The volume, the pressure and the temperature of the vapor filling this space were in all cases known, and from these data the weight of ammonia in the vapor space was calculated, assuming the laws of perfect gases to hold. While this is far from true for ammonia<sup>4</sup> at these high pressures, yet the error introduced was negligible, since the correction for ammonia in the vapor was in any case small compared with the total amount of ammonia present. This correction has been applied to the compositions given in Table II.

The temperatures given in Tables I, II and IV are subject to the corrections indicated in Table III, which were obtained by comparing the laboratory thermometer used in this investigation with a thermometer standardized by the Reichsanstalt.

TABLE I  
DETAILED DATA FOR A RUN

Run No. 6. Position of platinum point (transferred to steel tape), 22.917 ft.

Temperature of Thermostat <sup>a</sup> ° C.	Position of top of mercury column on steel tape Ft.	Height of mercury column Cm.	Average temp. of mercury column ° C.	Height of mercury column corrected for temp. <sup>b</sup> Cm.	Barometer corrected for temp. Cm.	Pressure of mixed xylene-ammonia vapors	
						Cm.	Atm.
8	20.375	77.48	23	77.19	72.89	150.08	1.975
10	20.167	83.82	25	83.49	72.92	156.41	2.058
12	19.962	90.07	25	89.71	72.98	162.69	2.141
14	19.750	96.53	26	96.11	72.97	169.08	2.224
15	19.641	99.85	26	99.43	72.97	172.40	2.268
17	19.416	106.70	26	106.25	72.98	179.23	2.358
20	19.078	117.00	26	116.52	72.99	189.51	2.493

<sup>a</sup> Temperature subject to corrections given in Table III.

<sup>b</sup> Corrections obtained from "Physikalische-Chemische Tabellen" by Landolt-Börnstein.

In Fig. 2 the pressures given in Table II are plotted as ordinates against the temperatures as abscissas. The horizontal portions of the isotherms represent the mean composition of the mixture for which 2 liquid phases are present. The end-points of the horizontal portions give the composition of the 2 liquid phases in equilibrium with each other. These points, at which the isotherms become horizontal, can be estimated only roughly from the plots. As it was desirable to know the composition of the 2 liquid phases somewhat more accurately, a separate set of experiments was carried out for their determination.

<sup>4</sup> Lange, *Z. angew. Chem.*, 1903, pp. 511-13.

TABLE II  
VAPOR PRESSURE AND MEAN COMPOSITION OF MIXTURES AT DIFFERENT TEMPERATURES

Temperature of thermostat ° C.	Pressure of mixed xylenes-ammonia vapors in atm.	Composition of the liquid phase Mol. per cent. ammonia	Pressure of mixed xylenes-ammonia vapors in atm.	Composition of the liquid phase Mol. per cent. ammonia	Pressure of mixed xylenes-ammonia vapors in atm.	Composition of the liquid phase Mol. per cent. ammonia
	Run 4		Run 5		Run 6	
8	4.64	31.0	3.32	17.5	1.97	9.5
10	4.89	30.9	3.47	17.4	2.06	9.5
12	5.15	30.9	3.59	17.3	2.14	9.5
14	5.43	30.8	3.76	17.3	2.22	9.4
15	5.56	30.8	3.85	17.2	2.27	9.4
17	5.86	30.8	4.01	17.2	2.36	9.3
20	6.30	30.7	4.27	17.1	2.49	9.3
	Run 8		Run 9		Run 11	
8	2.46	12.0	4.16	25.2	4.87	35.2
10	2.57	11.9	4.37	25.1	5.14	35.1
12	2.67	11.9	4.60	25.0	5.43	35.0
14	2.79	11.8	4.83	25.0	5.73	35.0
15	2.85	11.8	4.94	25.0	5.88	34.9
17	2.97	11.8	5.19	24.9	6.20	34.8
20	3.15	11.7	5.56	24.8	6.70	34.8
	Run 12		Run 13		Run 14	
8	5.01	38.1	5.18	42.6	5.29	46.1
10	5.31	38.1	5.49	42.5	..	..
12	5.61	38.0	5.81	42.5	..	..
14	5.92	37.9	6.14	42.3	6.30	46.1
15	6.10	37.9	6.31	42.2	6.46	45.9
17	6.40	38.0	6.68	42.4	..	..
20	6.93	37.9	7.31	42.2	..	..
	Run 15		Run 16		Run 17	
8	5.42	50.1	5.43	54.2	5.48	64.6
10	5.70	50.2	..	..	..	..
	Run 18		Run 19		Run 20	
8	5.48	78.1	5.50	86.5	5.51	89.1
10	5.86	78.1	5.87	86.5	5.88	89.1
12	6.25	78.1	6.28	86.6	6.29	89.1
14	6.66	78.1	6.70	86.6	6.70	89.1
15	6.89	78.0	6.91	86.5	6.93	89.1
17	7.34	78.0	7.36	86.4	7.39	89.1
20	8.06	78.0	8.10	86.4	8.10	89.1
	Run 21		Run 22		Run 23	
8	5.50	91.2	5.54	96.4	5.62	Pure ammonia
10	5.86	91.1	5.92	96.3	6.02	Pure ammonia
12	6.28	91.1	6.33	96.3	6.44	Pure ammonia
14	6.70	91.0	6.79	96.3	6.90	Pure ammonia
15	6.92	91.0	6.98	96.3	7.11	Pure ammonia
17	7.39	90.9	7.46	96.3	7.60	Pure ammonia
20	8.13	90.8	8.19	96.3	8.39	Pure ammonia

	Run 24		Run 26		Run 28	
8	5.60	98.7	5.50	95.1	5.37	50.2
10	6.00	98.7	5.88	95.0	..	..
12	6.41	98.7	6.30	95.0	..	..
14	6.86	98.7	6.73	95.0	..	..
15	7.09	98.7	6.95	95.0	..	..
17	7.56	98.7	7.41	95.0	..	..
20	8.33	98.7	8.18	95.0	..	..
	Run 30		Run 31		Run 32	
8	5.12	41.3	5.39	52.3	5.47	60.8
10	5.42	41.3	5.74	52.3	5.84	60.8
12	5.71	41.6	6.09	52.1	6.22	60.7
14	6.06	41.1	6.46	52.1	6.61	60.7
15	6.24	41.1	6.65	52.1	6.82	60.7
17	6.58	41.1	7.05	51.9	7.24	60.6
20	7.13	40.9	7.68	51.9	7.91	60.5
	Run 33		Run 34		Run 35	
8	5.49	67.5	5.50	73.4	5.53	80.2
10	5.86	67.4	5.88	73.4	..	..
12	6.26	67.4	6.28	73.4	..	..
14	6.67	67.4	6.69	73.4	..	..
15	6.88	67.3	6.91	73.4	..	..
17	7.31	67.3	7.35	73.4	..	..
20	8.01	67.3	8.06	73.4	..	..
	Run 36		Run 37			
8	5.53	81.8	5.51	83.4		
10	5.89	81.8	5.89	83.4		
12	6.30	81.8	6.28	83.4		
14	6.72	81.8	6.70	83.4		
15	6.94	81.8	6.92	83.4		
17	7.39	81.8	7.37	83.4		
20	8.12	81.8	8.10	83.4		

<sup>a</sup> All temperatures given in Table II are subject to the corrections given in Table III.

TABLE III  
THERMOMETER CORRECTIONS

Reading on laboratory thermometer °C.	Reading on Reichsanstalt's thermometer °C.	Reading on laboratory thermometer °C.	Reading on Reichsanstalt's thermometer °C.
8	7.83	15	14.79
10	9.82	17	16.79
12	11.81	20	19.80
14	13.79	..	...

### Composition of the Liquid Phases

**Apparatus.**—In Fig. 3 is shown the apparatus by means of which the composition of the 2 liquid phases was determined. In a preliminary experiment, the relative volumes of the 2 phases were determined by observations made on mixtures contained in a glass tube of uniform diameter. The mean composition of the liquid mixture used in this preliminary experiment corresponded to that at the critical point, *K*, which was esti-



mated from the plot shown in Fig. 2. The relative volumes of the 2 layers in the glass tube changed only a few per cent. for a temperature change from  $8^{\circ}$  to  $14.7^{\circ}$ , the temperature of the critical end-point. With this knowledge of the volumes occupied by the 2 phases of a mixture of known mean composition, the apparatus shown in Fig. 3 was designed. The volumes of the chambers A, B and C were so proportioned that, when in an upright position, the surface separating the two liquid layers should always come within the mid section B for temperatures from  $8^{\circ}$  to  $14^{\circ}$ .

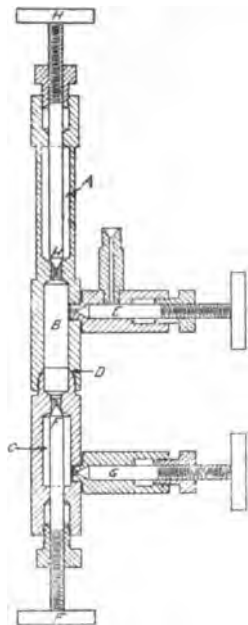


Fig. 3.—Apparatus employed in determining the composition of the liquid phases.

**Procedure.**—The procedure adopted in making a determination of the composition of the two liquid phases at a given temperature is as follows. The desired quantity of xylene was run into Chamber C from a weight pipet. The two parts of the apparatus were then screwed together at the conical joint D, and the whole was then placed in the thermostat in an upright position with Chamber C at the bottom. The outlet valve E was connected by means of a steel tube to the valve K, shown in Fig. 1. After evacuation, the desired quantity of ammonia was distilled into the apparatus. The quantity of ammonia introduced was obtained by difference in the weight of the container. Valve E was then closed and the whole apparatus was shaken at brief intervals, for a period of half an hour. The apparatus was then allowed to remain at rest for 10 or 15 minutes to allow thorough separation of the layers. Valve F was then closed, thus sealing a portion of the lower, heavier layer in Chamber C. A valve shown at G was next opened to allow for the expansion of the liquid due to temperature rise when the apparatus was removed from the bath. The valve H was then closed, sealing a portion of the upper, lighter layer in the chamber A. The apparatus was then removed from the bath, the portion in the mid section B was discarded through valve E, after which the two parts of the apparatus were separated at the conical joint D. Each portion of the apparatus was weighed. The ammonia in A and C was determined by running these portions into known quantities of standard sulfuric acid and titrating back with sodium hydroxide. The empty parts of the apparatus were then again weighed, and the weight of the sample of the liquid layer was obtained by difference.

**Experimental Results.**—The following are the data in detail as obtained in one of these determinations.

## EXPERIMENT 6 AT 12°

Wt. of part of apparatus containing upper portion of xylene-ammonia mixture.....	481.630 g.
Wt. of apparatus empty.....	480.326 g.
Wt. of sample of xylene-ammonia.....	1.304 g.
Vol. of 0.953 $NH_4SO_4$ neutralized by xylene-ammonia sample.....	49.89 cc.
Ammonia in sample.....	0.04760 mols $\approx$ 0.810 g.
Xylene in sample.....	0.494 g. $\approx$ 0.00467 mols
Mol per cent. of ammonia.....	90.3
Wt. of part of apparatus containing lower portion of xylene-ammonia mixture.....	429.648 g.
Wt. of apparatus empty.....	427.585 g.
Wt. of sample of xylene-ammonia.....	2.063 g.
Vol. of 0.953 $NH_4SO_4$ neutralized by xylene-ammonia sample.....	27.27 cc.
Ammonia in sample.....	0.0260 mols $\approx$ 0.442 g.
Xylene in sample.....	1.621 g. $\approx$ 0.0153 mols
Mol per cent. of ammonia.....	63.0

In Table IV are given the results of the determinations of the composition at 8°, 10°, 12° and 14°. In Fig. 2, these values of the composition are represented on their respective isotherms as points surrounded with circles.

TABLE IV  
COMPOSITION OF THE TWO LIQUID PHASES AT DIFFERENT TEMPERATURES

Run	Temp. °C.	$NH_3$ in upper layer %	$NH_3$ in lower layer %
12	8	93.7	56.5
13	8	93.4	56.8
14	8	93.4	56.8
3	10	92.0	60.5
4	10	92.4	60.3
5	10	91.7	59.5
15	10	92.3	60.4
6	12	90.3	63.0
7	12	90.3	64.0
11	12	90.9	64.3
8	14	87.2	..
9	14	87.2	71.8
10	14	88.1	71.8
Av.	8	93.6	56.7
Av.	10	92.2	60.4
Av.	12	90.5	63.8
Av.	14	87.5	71.8

The composition of the two liquid phases was determined at the boiling point of liquid ammonia at atmospheric pressure by means of another apparatus. In this experiment a known weight of xylene was run into a glass tube which was provided with a stirrer and which was immersed

in liquid ammonia contained in a Dewar flask. After exhausting, ammonia was distilled into the tube until 2 phases appeared, the liquid being vigorously stirred in the meantime. The amount of ammonia distilled over was determined by the change in the weight of the supply container. By this means the composition of the solution rich in xylene was determined.

To obtain the composition of the phase rich in ammonia, the above procedure was repeated, but with a small amount of xylene present at the beginning. The point was noted at which the xylene phase disappeared. From the known weights of xylene and ammonia present, the composition of the phase rich in ammonia was thus found.

It was difficult to determine accurately the appearance of a second phase or the disappearance of the first phase, and the results obtained in this part of the work may be in error by several per cent. The values found were 10.0 mol per cent. of ammonia for the phase rich in xylene, and 0.56 mol per cent. of xylene in the phase rich in ammonia.

The broken line curve shown in Fig. 2, passing through the circles on the isotherms, represents the composition of the liquid phases in equilibrium with each other.

### Discussion

The form of the pressure-concentration isotherms shown in Fig. 2 places the system ammonia:*meta*xylene among Büchner's first type,<sup>5</sup> in which the pressure of the 3-phase system lies intermediate between that of the pure components. In general, it has been found that liquid pairs having relatively high boiling points fall within this class, while liquid pairs whose boiling points are comparable fall within the class in which the pressure of the 3-phase system is higher than that of the components.

Büchner has found, as a result of an examination of a large number of systems of this type, that a temperature difference of at least 100° must exist between the boiling points of the two compounds, in order that they should fall within this class. There are, however, several exceptions to this rule. Büchner finds also that the ratio of the critical temperatures of the pairs which belong to this group has a value equal to, or greater than, 1.4. The system ammonia:xylene fulfils both these conditions, the difference in the boiling points being 172.7°, while the ratio of the critical temperatures is 1.41.

Considering the isotherms, the behavior of the mixtures of ammonia and xylene is such as might be expected. At temperatures below the critical end-point, the isotherms appear very much flattened at compositions approaching those of the 2 liquid phases. So, also, above the critical point, the isotherms at compositions in the neighborhood of the critical composition are comparatively flat. This system differs from other systems

<sup>5</sup> Ref. 2, p. 34.

most largely, perhaps, in that the critical region is relatively contracted on one side of the figure. Whereas in many cases the critical composition lies in the neighborhood of 50% of the 2 components, in this system the critical composition has a value of approximately 82 mol per cent. of ammonia. As may be seen from Fig. 2, the composition of the 2 liquid phases diverges largely at lower temperatures, so that at the boiling point of liquid ammonia the phase rich in xylene contains only 10 mol per cent. of ammonia while that rich in ammonia contains only 0.56 mol per cent. of xylene. From the form of the curve, it may be inferred that this system will not exhibit a lower critical end-point. In any case, the freezing point of ammonia is reached at a temperature of approximately  $-76^{\circ}$ , and a solid phase thus intervenes. It is doubtful, however, whether this system may be looked upon as having a lower critical end-point, even in the metastable regions.

Very striking is the large deviation of the pressure curves, which in this case are practically identical with the partial pressure curves of ammonia, from Raoult's law at low concentrations of xylene. It is theoretically necessary that, at the ammonia axis, the pressure curves shall become tangent to the straight line joining the pressure of this component with the origin on the opposite side of the diagram. It is evident, from the form of the curves, that the deviations from Raoult's law must be large even at relatively low concentrations. There is thus an intimate relation between the deviations from Raoult's law, that is to say, the deviations of a real system from that of an ideal one, and the appearance of new phases in the system. Our knowledge of the fundamental causes leading to a separation of a system into 2 phases is as yet too limited to enable us to interpret the phenomena observed, but it is clear, even now, that the appearance of new phases involves appreciable deviations from the laws of ideal systems. The greater the difference in the physical properties and constitution of the components in a mixture, the lower is the concentration at which the deviations from ideal systems reach appreciable values; and the lower is the concentration of the second component at which a new phase may appear. This is strikingly illustrated in the case of the system sodium:liquid ammonia, in which a critical phase appears having a composition of approximately 97 mol per cent. of ammonia.<sup>6</sup> This corresponds to a concentration a little above normal.

It follows from the theory of liquid mixtures that the isotherms in the homogeneous regions are two branches of a continuous curve, which represents the pressure of a homogeneous system over the complete concentration range. Between the compositions of the 2 liquid phases, however, the homogeneous states are metastable and unstable, and are therefore only realizable in part, excepting on the critical isotherm. It has not

<sup>6</sup> Kraus, *THIS JOURNAL*, 29, 1557 (1907). Ruff and Zedner, *Ber.*, 41, 1948 (1908).

been found possible thus far to evolve a theory of mixtures sufficiently general in nature to include the case of systems in which one or both of the components are abnormal liquids. It is clear, however, that the theoretical isotherm must exhibit a maximum and a minimum in this region. In the figure, the broken line connecting the points B and C indicates such a form of the curve. It may be inferred, since the isotherms immediately above the critical end-point as well as in the homogeneous regions adjacent to the 3-phase equilibrium are comparatively flat, that the theoretical isotherm throughout the metastable and unstable regions will be comparatively flat.

### Summary

1. The total vapor pressure of liquid mixtures of ammonia and *meta*-xylene has been determined for the entire range of compositions at temperatures of 8°, 10°, 12°, 14°, 15°, 17° and 20°. Mixtures of liquid ammonia and *meta*xylene exhibit a critical end-point at 14.7° at a pressure of 6.85 atmospheres and a composition of 81.4 mol per cent. of ammonia.
2. The composition of the liquid phases in equilibrium with each other in the 3-phase system has been determined at the temperatures given above and at -33.5°. At lower temperatures the percentage of ammonia in the phase rich in xylene decreases very markedly with the temperature.
3. The significance of the results obtained is briefly discussed.

WORCESTER, MASSACHUSETTS

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[CONTRIBUTION FROM THE GATES CHEMICAL LABORATORY OF THE CALIFORNIA INSTITUTE OF TECHNOLOGY, No. 14]

## THE COMPOSITION AND CRYSTAL STRUCTURE OF NICKEL NITRATE HEXAMMONIATE

By RALPH W. G. WYCKOFF<sup>1</sup>

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### 1. Introduction

When an excess of ammonia is added to a concentrated solution of nickel nitrate in water, faintly blue isotropic octahedra are obtained to which have been assigned the composition  $\text{Ni}(\text{NO}_3)_2 \cdot 4\text{NH}_3 \cdot 1$  (or 2)  $\text{H}_2\text{O}$ . By the slow cooling of a solution of appropriate concentration, large and perfect crystals of this salt are readily obtained. These crystals, however, decompose rapidly at room temperature, so that diffraction measurements were possible only after covering the crystal with a protecting coating of wax.

Comparison reflection spectra prepared in the usual manner<sup>2</sup> from a

<sup>1</sup> Member of the Staff of the Geophysical Laboratory of the Carnegie Institution of Washington.

<sup>2</sup> Wyckoff, *This JOURNAL*, **42**, 1100 (1920).

cleavage face of calcite (and of rock salt) and an octahedral face of one of these crystals, combined with its density, 1.46 as determined by a flotation-Westphal balance method, gave the following values of  $m/n^3$ , the ratio of the number  $m$  of chemical molecules in the unit cell, to the cube of the order of the reflection  $n$ .

$$m/n^3 = 4.34, \text{ if the composition is } \text{Ni}(\text{NO}_3)_2 \cdot 4\text{NH}_3 \cdot \text{H}_2\text{O},$$

$$m/n^3 = 4.07, \text{ if the composition is } \text{Ni}(\text{NO}_3)_2 \cdot 4\text{NH}_3 \cdot 2\text{H}_2\text{O}.$$

The first of these values does not correspond to any integral number of chemical molecules within the unit cube; the second is, however, in sufficiently close agreement with the value  $m = 4$ . It thus became evident that the first formula could not be a correct representation of the composition of these crystals. When, making the accustomed use of the results of the theory of space groups,<sup>3</sup> a plausible structure containing 4 molecules of  $\text{Ni}(\text{NO}_3)_2 \cdot 4\text{NH}_3 \cdot 2\text{H}_2\text{O}$  within the unit was sought, it was found that none was possible. The incorrectness of the two assigned compositions of this salt, which thus became apparent, led to the following analyses.

## 2. Analysis of the Nickel Nitrate Hexammoniate

It was assumed that the crystals have the composition  $\text{Ni}(\text{NO}_3)_2 \cdot x\text{NH}_3 \cdot y\text{H}_2\text{O}$ . Proceeding upon this basis two analyses were made: (1) a determination of the ammonia content, and (2) a determination of the amount of substance volatilized by ignition to nickel oxide (NiO). The amount of ammonia was obtained by adding a weighed portion of the salt directly to a known amount of standard hydrochloric acid solution and titrating back the excess of acid with standard alkali, using methyl red as indicator. The correctness of this direct titration was assured through comparison with an analysis by a Kjeldahl distillation.

The samples were prepared by the following procedure. The salt was precipitated as a fine powder by the addition of an excess of ammonium hydroxide to a cold conc. solution of nickel nitrate. This precipitate was collected, washed repeatedly and rapidly, first with alcohol and then with ether, and kept in a refrigerated desiccator for at least 12 hours before weighing, in order that the salt might become free from ether. In this manner a constant weight was attained. After washing, the temperature of the salt was not allowed to rise above  $0^\circ$  until immediately before use.

Two determinations of the ammonia content gave 35.65% and 35.58% in the salt. The theoretical percentage for  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{NH}_3$  is 35.87%.

Two determinations of the loss on igniting the salt to nickel oxide resulted as follows.

(1)	(2)	(3)	(4)	(5)
Wt. sample	Wt. NiO	Wt. $\text{Ni}(\text{NO}_3)_2$	"Volatile matter"	"Volatile matter"
G.	G.	(calc. from (2))	(1) minus (3)	%
0.3719	0.0977	0.2390	0.1329	35.73
0.2034	0.0534	0.1306	0.0728	35.76
Theoretical "Volatile matter" in $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{NH}_3$				35.87

<sup>3</sup> Wyckoff, *Am. J. Sci.*, 1, 127 (1921), etc.

From these two sets of experiments it is clear that the true composition of these crystals is  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{NH}_3$ .

### 3. The Crystal Structure of the Nickel Nitrate Hexammoniate

As already indicated, reflection spectra from the octahedral face showed that 4 molecules of  $\text{Ni}(\text{NO}_3)_2 \cdot 4\text{NH}_3 \cdot 2\text{H}_2\text{O}$  could be associated with the unit cube. The molecular weights of ammonia and of water are nearly equal so that the same calculation shows that either 4 or 32 molecules of  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{NH}_3$  must be contained within the unit cell. With 4 molecules, the length of the side of this unit becomes 10.96 Å. U. ( $10.96 \times 10^{-8}$  cm.).

The analysis of a series of Laue photographs with the incident X-rays roughly normal to octahedral faces and the subsequent determination of structure were carried out by methods already described.<sup>4</sup>

TABLE I  
LAUE PHOTOGRAPHIC DATA<sup>a</sup> FOR  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{NH}_3$

Appearing planes			Absent planes			
Indices of reflecting plane	Relative spacing	Wave length	Estimated intensity	Indices of reflecting plane	Relative spacing	Wave length
$\bar{5}\bar{1}\bar{3}$	0.169	0.427	10	$\bar{4}50$	0.156	0.498
$\bar{5}\bar{1}\bar{5}$	0.140	0.397	7	$\bar{4}2\bar{5}$	0.149	0.475
$\bar{5}\bar{5}\bar{1}$	0.140	0.376	6	$\bar{3}6\bar{2}$	0.143	0.497
$\bar{3}\bar{5}\bar{5}$	0.130	0.429	7	$\bar{4}6\bar{1}$	0.137	0.422
$\bar{5}\bar{5}\bar{3}$	0.130	0.458	7+	$\bar{1}6\bar{4}$	0.137	0.488
$\bar{1}\bar{3}\bar{7}$	0.130	0.440	2	$\bar{5}2\bar{5}$	0.136	0.419
$\bar{3}\bar{7}\bar{3}$	0.122	0.397	2	$\bar{0}6\bar{5}$	0.128	0.451
$\bar{1}\bar{7}\bar{5}$	0.115	0.386	2	$\bar{5}6\bar{0}$	0.128	0.358
$\bar{5}\bar{1}\bar{7}$	0.115	0.417	4	$\bar{7}\bar{1}\bar{4}$	0.123	0.438
$\bar{5}\bar{7}\bar{1}$	0.115	0.323	0.5	$\bar{2}\bar{7}\bar{4}$	0.120	0.396
$\bar{7}\bar{5}\bar{5}$	0.100	0.400	1	$\bar{4}\bar{7}\bar{2}$	0.120	0.369
$\bar{1}\bar{5}\bar{9}$	0.096	0.430	0.5	$\bar{7}\bar{1}\bar{6}$	0.107	0.395
$\bar{9}\bar{1}\bar{5}$	0.096	0.400	0.1	...	...	...
$\bar{2}\bar{2}\bar{1}$	0.333	0.947	10	...	...	...
$\bar{1}\bar{2}\bar{2}$	0.333	0.828	8	...	...	...
$\bar{3}\bar{2}\bar{0}$	0.277	0.773	4	...	...	...
$\bar{3}\bar{2}\bar{2}$	0.242	0.771	2	...	...	...
$\bar{3}\bar{3}\bar{2}$	0.213	0.849	3	...	...	...
$\bar{4}\bar{3}\bar{1}$	0.196	0.770	0.5	...	...	...
$\bar{5}\bar{1}\bar{2}$	0.182	0.865	0.1	...	...	...
$\bar{3}\bar{5}\bar{0}$	0.171	0.966	0.1	...	...	...
$\bar{4}\bar{3}\bar{3}$	0.171	0.773	0.5	...	...	...

<sup>a</sup> Only typical data from a single photograph are recorded in this table. The estimated intensities are not to be considered as furnishing more than a general idea of the intensities of the various diffraction spots.

The characteristics of the Laue photographs furnished by this salt are almost identical with those given by the photographs from the hexammo-

<sup>4</sup> Wyckoff, *Am. J. Sci.*, **50**, 317 (1920). Wyckoff and Posnjak, *THIS JOURNAL*, **43**, 2292 (1921).

niates of the nickel halides.<sup>5</sup> No planes were found to reflect in the first order region except those having all odd indices. Furthermore, the intensity peculiarities of these all odd planes closely resemble those of the halides. The nature of the data obtained from these photographs will be seen from Table I. In the double endeavor to increase the number of reflections found in the Laue photographs and particularly to bring out spots in the first order having other than all odd indices, exposures three to four times as long as usual were made; but for the first purpose these long exposures had little success, and in the second regard they failed utterly.

In order to preserve the existence of  $\text{NH}_3$  as a distinct grouping of atoms, it was necessary to assign the hexammoniate halides<sup>5</sup> to the paramorphic hemihedry (pyritohedral class) of the cubic system. The same is true for this salt. It is thus apparent that this crystal must have the symmetry of one of the three paramorphic space groups permitting 4 molecules within the unit cube,  $T_h^2$ ,  $T_h^3$  and  $T_h^6$ . Methods are at hand for distinguishing among these three space groups on the basis of the Laue photographic data to which they give rise, as will be shown in detail in a subsequent publication. These methods are applicable to the present case because there are 24 oxygen atoms and because the first and last of these space groups, being built upon a simple cubic lattice, have 24 as the maximum number of equivalent positions within the unit cell. The fact that only all odd planes are found in the first order would assign this crystal to  $T_h^3$ , the space group corresponding to the hexammoniate halides. As reference to this previous work will show, the arrangement of the atoms in  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{NH}_3$  would then have to be as follows: Nickel, arrangement 4(b); Nitrogen (nitrate), 8(e); Nitrogen (ammonia), 24 (c); Oxygen, 24(a) or 24(c) with a value of  $u$  different from that of the ammonia nitrogen atoms; Hydrogen, one grouping of atoms at 24(c) with a still different value of  $u$ , and one grouping of 48 equivalent atoms.

Both of these possible positions for the oxygen atoms not only require that the distance between nitrate nitrogen atoms and oxygen atoms should be very much greater than the corresponding distance found in sodium nitrate,<sup>6</sup> but they also destroy the nitrate group itself. In view of these surprising results it seems desirable to see whether special values cannot be given to the coördinate positions of atoms in either  $T_h^3$  or  $T_h^6$  which permit the arrangements thus resulting likewise to conform with the diffraction data. By following an orderly procedure it can be shown that, though  $T_h^2$  cannot be made to approach a face-centered structure, appropriate coördinate values can be found for the space group  $T_h^6$ .

<sup>5</sup> Ralph W. G. Wyckoff, *THIS JOURNAL*, **44**, 1239 (1922).

<sup>6</sup> W. L. Bragg, *Proc. Roy. Soc.*, **89A**, 468 (1914). Wyckoff, *Phys. Rev.*, [2] **16**, 149 (1920).



The most generally placed equivalent positions of  $T_h^6$  are as follows.<sup>7</sup>

Twenty-four equivalent positions within the unit:

$$\begin{aligned} &xyz; x+\frac{1}{2}, \frac{1}{2}-y, \bar{z}; \bar{x}, y+\frac{1}{2}, \frac{1}{2}-z; \frac{1}{2}-x, \bar{y}, z+\frac{1}{2}; \\ &zxy; \bar{z}, x+\frac{1}{2}, \frac{1}{2}-y; \frac{1}{2}-z, \bar{x}, y+\frac{1}{2}; z+\frac{1}{2}, \frac{1}{2}-x, \bar{y}; \\ &yxz; \frac{1}{2}-y, \bar{z}, x+\frac{1}{2}; y+\frac{1}{2}, \frac{1}{2}-z, \bar{x}; y, z+\frac{1}{2}, \frac{1}{2}-x; \\ &\bar{x}\bar{y}\bar{z}; \frac{1}{2}-x, y+\frac{1}{2}, z; x, \frac{1}{2}-y, z+\frac{1}{2}; x+\frac{1}{2}, y, \frac{1}{2}-z; \\ &\bar{z}\bar{x}\bar{y}; z, \frac{1}{2}-x, y+\frac{1}{2}; z+\frac{1}{2}, x, \frac{1}{2}-y; \frac{1}{2}-z, x+\frac{1}{2}, \bar{y}; \\ &\bar{y}\bar{z}\bar{x}; y+\frac{1}{2}, z, \frac{1}{2}-x; \frac{1}{2}-y, z+\frac{1}{2}, x; y, \frac{1}{2}-z, x+\frac{1}{2}. \end{aligned}$$

The following special positions reduce the number of equivalent positions.

Eight equivalent positions:

8(h):

$$\begin{aligned} &uuu; u+\frac{1}{2}, \frac{1}{2}-u, \bar{u}; \bar{u}, u+\frac{1}{2}, \frac{1}{2}-u; \frac{1}{2}-u, \bar{u}, u+\frac{1}{2}; \\ &\bar{u}\bar{u}\bar{u}; \frac{1}{2}-u, u+\frac{1}{2}, \bar{u}; u, \frac{1}{2}-u, u+\frac{1}{2}; u+\frac{1}{2}, u, \frac{1}{2}-u; \end{aligned}$$

Four equivalent positions:

$$4(b): 000; 0\frac{1}{2}\frac{1}{2}; \frac{1}{2}\frac{1}{2}0; \frac{1}{2}0\frac{1}{2}.$$

$$4(c): \frac{1}{2}\frac{1}{2}\frac{1}{2}; \frac{1}{2}00; 00\frac{1}{2}; 0\frac{1}{2}0.$$

It is readily seen that by assigning to  $u$  the value  $1/4$ , both the nickel atoms and the nitrate nitrogen atoms will occupy identically the same positions that they have in the arrangement deducible from  $T_h^3$ ; they consequently will contribute nothing to first order reflections from planes having other than all odd indices. By an appropriate equating of the coefficients in the intensity expressions for the most general positions of equivalent atoms, all of the particular values of  $x$ ,  $y$ , and  $z$  which will permit of first order reflections from all odd planes can be found. These prove to be identical with the two special cases of 24 equivalent positions which are derivable from the space group  $T_h^3$ . They consequently introduce no new possibilities.

Two alternatives are presented. One consists in taking the diffraction data at their face value and assigning  $Ni(NO_3)_2 \cdot 6NH_3$  to the space group  $T_h^3$  in view of the complete absence of first order reflections except from all odd planes; but it has been pointed out that such an arrangement of the atoms destroys the identity of the nitrate group by its equal association of 6 oxygen atoms with each nitrogen atom. The other alternative is to assume that first order reflections from planes having even indices really exist, but with an intensity too faint to be detected in the Laue photographs. This crystal would then have the symmetry of the space group  $T_h^6$ , with atomic positions either identical with or closely approximating those arising from  $T_h^3$ . According to this arrangement the nickel atoms are to be found at the positions of 4(b), the nitrate nitrogen atoms at 8(h), and the ammonia nitrogen and the oxygen atoms in

<sup>7</sup> The designations employed are those used in the writer's book entitled "An Analytical Representation of the Theory of Space Groups" shortly to be published by the Carnegie Institution of Washington.

general positions. In order to satisfy the diffraction data, it is necessary that the value of  $u$  for the nitrate nitrogen atoms be approximately  $1/4$ , and that the ammonia nitrogen atoms be either exactly in, or very close to, the positions designated by the coördinate values  $v00$ , where  $v$  is somewhat less than 0.25. This is in accord with the relation between the nickel atom and its coördinated ammonia molecules as deduced from a study of the hexammoniate halides. The absence of strong first order reflections from other than all odd planes and of any observable dissymmetry in the photograph (such as is apparent in the photographs of crystals having pyritohedral symmetry) suggests that the oxygen atoms should not deviate far from the positions  $1/4^1/40$ . The same procedure which showed that arrangements 24(a) and 24(c) arise from  $T_h^6$  indicates that, because  $2/3$  of the atoms destructively interfere with one another in the first order, the intensity of reflection from an arrangement having the coördinate values  $1/4^1/4v'$  is particularly slight. It consequently becomes apparent that, if this second alternative is the correct one, the oxygen atoms cannot vary greatly from the positions designated by  $1/4^1/4v'$ . Calculations of intensity were carried out in the usual manner for different values of  $u$  for the nitrate nitrogen atoms and of  $v'$  for the oxygen atoms; a comparison of such calculated intensities with those of planes actually appearing in the photographs indicates that both  $u$  and  $v'$  may have a considerable range about the positions  $u = 1/4$  and  $v' = 0$  without the amplitudes which they might contribute to first order reflections being significant.

There is good reason for believing that this second alternative is the correct one. Barium and strontium nitrates give crystals which upon the basis of the diffraction data they furnish have been assigned<sup>8</sup> to the space group  $T_h^6$ . In connection with the present work Laue photographs of both barium and strontium nitrate have been examined with results which agree with the previous ones in ascribing them to this space group. Diffraction data from crystals of  $Zn(BrO_3)_2 \cdot 6H_2O$  and  $Ni(ClO_3)_2 \cdot 6H_2O$ , taken as substances similar in nature to the compound under investigation,<sup>9</sup> agree in assigning both of these crystals definitely to this space group  $T_h^6$ . It consequently seems probable that  $Ni(NO_3)_2 \cdot 6NH_3$  also has the symmetry of  $T_h^6$  with such values of the coördinate positions of its atoms as to make it approach closely to a truly face-centered structure. Accordingly, the positions of the atoms within a unit cell of this crystal are as follows: Nickel, arrangement 4(b); Nitrogen (nitrate), 8(h), with a value of  $u$ , the variation of which from  $u = 1/4$  may be appreciable; Nitrogen (ammonia), general positions but with values of the coördinates equal or close to  $x = v$ ,  $y = 0$ ,  $z = 0$ , where  $v$  has a value somewhat less than 0.25; Oxygen, general positions but with values of the coördinates

<sup>8</sup> Nishikawa and Hudinuki, *Proc. Tokyo Math. Phys. Soc.*, [2] 9, 197 (1917).

<sup>9</sup> A brief discussion of the structures of these crystals will be given in a later paper.

probably close to  $x = 1/4$ ,  $y = 1/4$ ,  $z = v'$ , where the variation of  $v'$  from zero cannot be ascertained with accuracy; Hydrogen, three sets of general positions which group the three hydrogen atoms about each ammonia nitrogen atom.

The structure thus assigned to  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{NH}_3$  is like that possessed by  $\text{NiCl}_2 \cdot 6\text{NH}_3$  with nitrate groups replacing the chlorine atoms, except that the centers of the nitrate groups *may* be displaced along the body diagonals of the unit much as are the sulfur atoms in pyrites.

Structures which are at all probable in a chemical sense and which involve an atomic equivalence different from that here assumed (such, for example, as those arising from the assumption that two of the oxygen atoms of a nitrate group are different from the third), cannot be made to conform with the experimental data. Neither is it apparent that anything is to be gained by assuming that 32 molecules, instead of 4, are contained within the unit cube.

### Summary

From X-ray spectrum measurements and space group reasoning it can be shown that the crystals formed on the addition of ammonia to a solution of nickel nitrate cannot have the composition usually ascribed to them. Careful chemical analysis proves them to be  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{NH}_3$ . A study of the Laue photographs of these crystals by the generally applicable methods which use the theory of space groups indicates that they have a structure similar to that of the previously studied nickel hexammoniate halides with nitrate groups replacing the halogen atoms, and the ammonia groups related to the nickel atoms in the same manner in both compounds. The positions of the atoms of the nitrate groups cannot, however, be determined with great accuracy. Both the symmetry characteristics and the diffraction data permit the same kind of displacement of the nitrate nitrogen atoms as is experienced by the sulfur atoms in pyrites. The length of the side of the unit cube has been determined as 10.96 Å. U.

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[CONTRIBUTION FROM THE COBB CHEMICAL LABORATORY OF THE UNIVERSITY OF VIRGINIA]

## RAPID ELECTROLYSIS WITHOUT ROTATING ELECTRODES

By GRAHAM EDGAR AND R. B. PURDUM

Received April 13, 1922

### Introduction

Within recent years various methods of "rapid electrolysis" for the estimation of metals have been developed and have become widely used. An extensive bibliography seems unnecessary, but it may be noted that Gooch and Medway<sup>1</sup> proposed rotation of the cathode; Exner<sup>2</sup> proposed rotation of the anode; Fischer<sup>3</sup> showed that vigorous stirring of the electrolyte by any means achieved the desired result; and Frary<sup>4</sup> utilized the effect of a magnetic field to stir the electrolyte. The present paper describes a simple glass apparatus in which stirring of the electrolyte is effected indirectly by a current of air, and with which results have been obtained, as rapid and as accurate as those afforded by the use of rotating electrodes.

### Description of Apparatus

Preliminary experiments were carried out in a glass cylinder with a cathode of platinum gauze and an anode of coiled platinum wire, the electrolyte being stirred by a current of air bubbled through the liquid. The results were not altogether satisfactory, and it was obvious that the stirring was not uniform, and that the fine bubbles of gas liberated at the electrodes had a tendency to form a spray which was carried out of the cylinder by the air current, causing loss of the solution. Furthermore, there seemed to be the possibility, in some cases at least, of causing oxidation by exposing the cathode to the air.

After a number of trials the apparatus illustrated in Fig. 1 was developed, which has proved altogether satisfactory.<sup>5</sup>

It consists essentially of a tube of Pyrex glass (31 mm. in diameter) to which are sealed 3 glass "air lifts,"

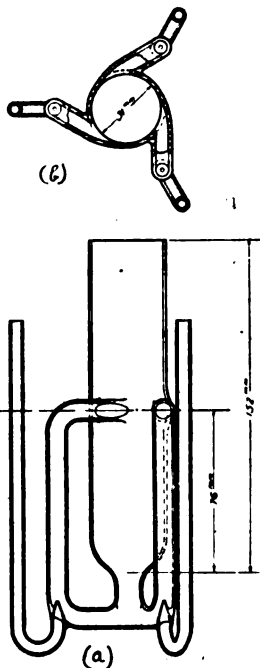


Fig. 1.

<sup>1</sup> Gooch and Medway, *Am. J. Sci.*, [IV] 15, 320 (1903).

<sup>2</sup> Exner, *THIS JOURNAL*, 25, 896 (1903).

<sup>3</sup> Fischer, *Z. angew. Chem.*, 20, 138 (1907).

<sup>4</sup> Frary, *Z. Elektrochem.*, 13, 308 (1907).

<sup>5</sup> This apparatus may be purchased from Messrs. Eimer and Amend, 205 Third Ave., New York City.

connecting in a single tube at the bottom, and entering symmetrically about half way up the wide tube, the upper seals being made tangentially. Fig. 1 (a) shows 1 of the 3 air lifts in detail, and Fig. 1 (b), which is a cross-section through the apparatus at the level of the upper entrance of the side tubes into the wide tube, illustrates the general plan.

If this apparatus is half filled with liquid and a current of air is forced (or drawn by suction) through the injectors, it is quite obvious that stirring is effected in two ways. In the first place, a continuous current of liquid is carried upward by the air lifts, causing vertical stirring; in the second, this liquid (with the air bubbles) is delivered into the wide tube in such a way as to cause rotational stirring. By suspending fine solid particles in the liquid it can be seen that the rotational stirring is very rapid, while the vertical movement is also considerable. Furthermore, the air bubbles are thrown centrifugally against the walls of the cell, so that no spray is carried out, even when a rapid air current is employed. In using the cell for an electrolytic determination the wide tube is fitted with a rubber stopper carrying a glass tube and the electrodes. These consist of a cylindrical platinum gauze cathode ( $2.5 \times 5$  cm., having about 50 sq. cm. surface) and a spiral platinum wire anode.

### Experimental Technique

In carrying out a determination the following technique has been employed.

Rubber caps are slipped over the air inlets (to prevent the solution from running back into them), the solution to be electrolyzed is introduced, the stopper with its electrodes is inserted, the exit tube is connected to a water aspirator and suction is applied. The caps are then removed and a little water is added from a wash-bottle to each of the air inlets to rinse out any liquid which may have run back into them. The level of the solution is adjusted so that it just reaches the level of the upper entrance of the air lifts while the air current is flowing. The electric circuit is then closed. When the electrolysis is nearly complete the suction is increased for a moment to wash down the walls of the vessel, and is then reduced to the normal flow. At the end of the electrolysis the stopper is lifted and the electrodes are washed partially with a jet of water from a wash-bottle, without breaking the current. They are then transferred at once to a beaker of water, washed thoroughly with water, then with alcohol, and are finally dried as usual and weighed.

Most of the actual determinations have been made upon solutions of copper sulfate, to which have been added acids, ammonia, salts, etc., in varying amounts, as in the customary analytical procedures for electrolysis with rotating electrodes. Determinations have also been made of copper in the presence of zinc and lead, and a few estimations of other

metals<sup>8</sup> have been included as shown in the table. Characteristic experimental data are given in Table I. Carefully standardized solutions, calibrated volumetric apparatus and weights were employed, and all ordinary precautions of good analytical work were taken. The 110-volt lighting circuit, reduced by resistance lamps was used as the source of current.

TABLE I  
TOTAL VOLUME OF SOLUTION, 60 Cc.

Metal present	Metal found	Error	Current	Time	Reagent added	Other metals present	Solution becomes colorless
G.	G.	G.	Amps. <sup>a</sup>	Min.	Cc.	G.	Min.
Cu							
Conc. HNO <sub>3</sub>							
0.1983	0.1982	-0.0001	0.5	60	3	...	20
0.1983	0.1984	+0.0001	1.0	30	3	...	12
0.1983	0.1981	-0.0002	3.0	15	3	...	4
0.1983	0.1982	-0.0001	2.0	20	3	0.1 Zn	5
0.1983	0.1982	-0.0001	3.0	15	3	0.1	4
0.1983	0.1983	±0.0000	3.0	15	3	0.2	4
0.1983	0.1982	-0.0001	2.0	20	1	0.1	5
0.1983	0.1984	+0.0001	2.0	25	5	0.1	5
0.3966	0.3968	+0.0002	3.0	20	3	...	6-7
0.1983	0.1984	+0.0001	1.0	25	3	{ 0.1 Zn 0.003 Pb	8-10
Conc. H <sub>2</sub> SO <sub>4</sub>							
0.1983	0.1983	±0.0000	1.0	20	1	...	7
0.1983	0.1985	+0.0002	2.0	15	2	...	3-4
0.1983	0.1985	+0.0002	3.0	10	2	...	2
0.1983	0.1984	+0.0001	1.0	25	2	0.1 Zn	7
Conc. NH <sub>4</sub> OH							
0.1983	0.1985	+0.0002	2.5	15	6	...	8
Zn							
0.1833	0.1834	+0.0001	2.0	30	NaOH 4.5 g.	...	..
Fe							
0.1896	0.1898	+0.0002	3.0	30	{ (NH <sub>4</sub> ) <sub>2</sub> C <sub>2</sub> O <sub>4</sub> 5 g.	...	20
Fe							
0.1890	0.1888	-0.0002	3.0	30	{ H <sub>2</sub> C <sub>2</sub> O <sub>4</sub> ·2H <sub>2</sub> O 0.3 g.	...	20
Ni							
0.1999	0.1998	-0.0001	3.5	15	{ Conc. NH <sub>4</sub> OH 25. cc.	...	8
Ni							
0.1999	0.1999	±0.0000	3.5	20	{ (NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> 1.5 g.	...	8

<sup>a</sup> Since the surface of the cathode was about 50 sq. cm. the current density (N.D.<sub>100</sub>) is given approximately by multiplying these figures by 2.

Inspection of the data shows that the time necessary for a determination and the accuracy of the results obtained, compare favorably with those obtained with rotating electrodes, under a wide variety of experimental conditions.

<sup>8</sup> In addition to the data recorded in Table I, satisfactory determinations have been made of Ag, Co, Cd and Pb.

### Summary

A simple glass apparatus for electro-analysis has been described in which the solution is stirred indirectly by a current of air, and in which rapid electrolytic determinations may be made.

Data illustrating applications of the apparatus are presented.

UNIVERSITY, VIRGINIA

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[CONTRIBUTION FROM THE KENT CHEMICAL LABORATORY OF THE UNIVERSITY OF CHICAGO]

## THE MOLECULAR REARRANGEMENT OF SYMMETRICAL BIS-TRIPHENYLMETHYLHYDRAZINE

BY JULIUS STIEGLITZ AND RALPH L. BROWN<sup>1</sup>

Received September 7, 1921

Organic hydrazine derivatives resemble derivatives of hydroxylamine in all fundamental characteristics, except that, with a single exception, they have not been found to undergo molecular rearrangements of the same type as the Beckmann rearrangement of oximes or the Lossen rearrangement of hydroxamic acids. Stieglitz and Senior,<sup>2</sup> who called attention to this difference, made a series of attempts to effect such rearrangements of hydrazine compounds, but all their efforts were unsuccessful except when they used *sym.*-bis-triphenylmethylhydrazine,  $(\text{C}_6\text{H}_5)_3\text{C}.\text{NH}.\text{NH}.\text{C}(\text{C}_6\text{H}_5)_3$ . When they heated this compound to  $250^\circ$  to  $300^\circ$  with anhydrous zinc chloride and hydrolyzed the reaction product, aniline was obtained, which proved conclusively that one of the phenyl groups of the triphenylmethyl radicals migrates under these conditions from carbon to nitrogen, which is the typical shift of the Beckmann-Lossen rearrangements, and of the analogous rearrangements in the triphenylmethane series discovered by the one of us and his collaborators.<sup>3</sup> The only other product identified in the preliminary investigation was triphenylmethane, a product of a parallel thermal decomposition of the hydrazine.

The present paper reports the results of a continuation of the investigation, which was carried out to throw light on the mechanism of the rearrangement. Unexpected results obtained toward the end of the investigation have made it impossible, at the present moment, to give a complete theory of the reaction, but as the one of us (Brown) was called to service in the U. S. Army, we wish to present now the lines of thought

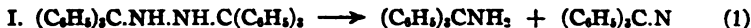
<sup>1</sup> This report forms the basis of a dissertation submitted by Ralph L. Brown in part fulfilment of the requirement for the degree of Doctor of Philosophy at the University of Chicago, 1917.

<sup>2</sup> *Proc. Nat. Acad. Sci.*, **1**, 207 (1915); and *THIS JOURNAL*, **38**, 2727 (1916).

<sup>3</sup> See the literature references in *THIS JOURNAL*, **36**, 272 (1914) and **38**, 2051 (1916).

followed as working hypotheses and the relation of the results obtained, to these views.

By analogy to other rearrangements of this type, two possible courses of the rearrangement reaction are suggested at the outset.<sup>4</sup> In the first place, according to the theory of the one of us,<sup>5</sup> we might have as the primary action offering least resistance a decomposition of the hydrazine compound into triphenyl-methylamine and triphenyl-methylimide, a univalent nitrogen compound which would undergo the rearrangement proper



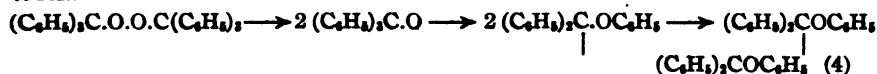
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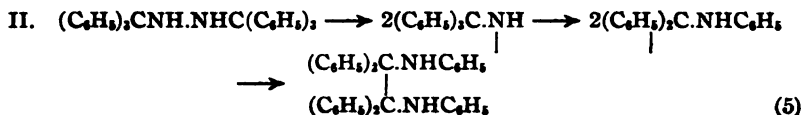
By hydrolysis of the phenylimido-benzophenone thus formed, aniline and benzophenone would be produced.



The alternative course of the reaction would be a rearrangement akin to the rearrangement of triphenylmethyl-peroxide, as investigated by Wieland.<sup>6</sup>



*Bis*-triphenylmethylhydrazine might rearrange in an analogous way as follows.



Hydrolysis of the resulting product, if it occurred at all, would lead to the formation of aniline and benzopinacone.



In the experimental part of this report, it will be shown that, besides aniline, which was again identified after hydrolysis of the reaction product, *benzophenone* was isolated and identified, a result which decidedly favors the mechanism of the reaction expressed under I. The third product of the reaction required by Scheme I is triphenyl-methylamine. This was not found, but it was suspected that any triphenyl-methylamine formed would be decomposed by the zinc chloride at the temperature of the reaction. For that reason, the effect of zinc chloride on the amine was studied. As anticipated, when triphenyl-methylamine reacts with zinc

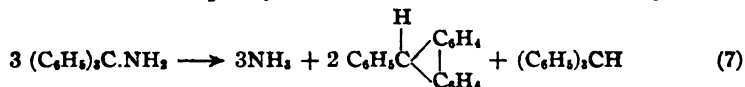
<sup>4</sup> The interpretation from the point of view of the electron conception of valence will be given further on in this paper.

<sup>5</sup> See the literature references given by Stieglitz and Leech, *THIS JOURNAL*, **36**, 272 (1914) and by Stieglitz and Stagner, *ibid.*, **38**, 2051 (1916).

<sup>6</sup> Wieland, *Ber.*, **44**, 2550 (1911).



chloride, the chief products of decomposition are ammonia, phenyl-diphenylenemethane and triphenylmethane. For instance, we may have

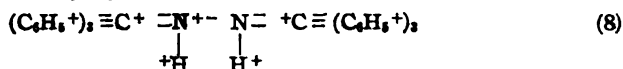


This action is analogous to the decomposition of triphenylmethyl chloride and bromide by heat and of the corresponding carbinol by phosphorus pentoxide.

Returning now to the examination of the products of the rearrangement of *bis*-triphenylmethylhydrazine, we have found without difficulty that ammonia and phenyl-diphenylenemethane, besides triphenylmethane, are indeed formed in the reaction. Furthermore, quantitative determinations, which will be discussed at greater length presently, showed that the amount of ammonia, *i. e.*, triphenyl-methylamine as the primary product formed is of the order demanded by the equations given under I.

Thus far, all the experimental evidence, therefore, favors the conception that the rearrangement of *bis*-triphenylmethylhydrazine by zinc chloride follows the course through a univalent nitrogen derivative which seems to be the same as that commonly followed as the path of least resistance<sup>7</sup> in the rearrangement of oximes, hydroxamic acids, chloro- and bromo-amides of the acids, acyl azides, triarylmethyl-azides, -hydroxylamines and -chloro-amines, as grouped together by the theory of the one of us. Exhaustive examination of the reaction products brought to light further facts, some of which have raised novel and interesting questions. Before these are presented, it seems wisest to complete the discussion of the rearrangement proper by referring as briefly as possible to the interpretation of the rearrangement from the point of view of the electron conception of valence.<sup>8</sup> The discussion from this fundamental point of view will greatly facilitate the consideration of the further experimental results to be presented below.

For *bis*-triphenylmethylhydrazine we have the electronic structure<sup>9</sup>



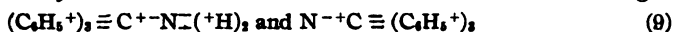
The atom with an unstable positive charge, as postulated by the one of us as occurring in all of the rearranging compounds of this character, in the present instance is one of the two otherwise apparently symmetrical nitrogen atoms: for the sake of convenience we have designated the unstable nitrogen atom with the positive charge in question by putting it in heavy type as **N**<sup>+</sup>. In the formation of a rearranging univalent nitrogen derivative, either of the following courses may be followed:

<sup>7</sup> Stieglitz, *Proc. Nat. Acad. Sci.*, Ref. 2. Stieglitz and Stagner, Ref. 5.

<sup>8</sup> Stieglitz and Leech, Ref. 5. Jones, *Am. Chem. J.*, **50**, 440 (1913).

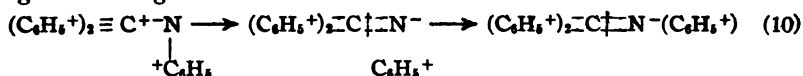
<sup>9</sup> Only those charges are indicated which bear on the discussion.

(1) the true ammonia nitrogen atom  $\text{N}^-$  deprives the nitrogen atom  $\text{N}^+$  of its hydrogen atom, forming triphenylmethyl-amine  $(\text{C}_6\text{H}_5)_3\text{C}.\text{NH}_2$  and triphenylmethyl-imide  $(\text{C}_6\text{H}_5)_3\text{C}.\text{N}^+$  which by a shift of the electron would form  $(\text{C}_6\text{H}_5)_3\text{C}.\text{N}$ ; (2) more probably the disturbance originates in the unstable nitrogen atom  $\text{N}^+$  which captures 2 electrons from the neighboring nitrogen atom. With the accompanying migration of the hydrogen atom lost by  $\text{N}^-$  as a result of the loss of its electrons, this gives



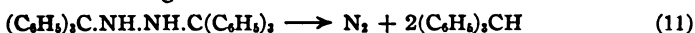
As a basis of choice between these two possible courses we have no experimental information except that the second course would be exactly analogous to the changes occurring in the closely related rearrangements of halogen amides, oximes, etc. A final decision between these two paths would be, we believe, of great importance, since therein most likely will be found the key to the interesting fact that this symmetrical hydrazine rearranges, whereas all the unsymmetrical hydrazines examined by Senior and the one of us are not rearranged.<sup>10</sup>

In either case, we have then, further, the normal course for univalent nitrogen rearrangements<sup>11</sup>



Two electrons migrate from the methyl carbon from the valence indicated by the sign in heavy type to the univalent nitrogen atom, the released positive phenyl group migrating to the free negative charge on the nitrogen.

Returning now to the further observations made in the course of the experimental work, we would mention first that the formation of triphenylmethane and nitrogen



observed by Senior and the one of us, was conclusively shown to be a thermal decomposition. The electronic interpretation is given in the preliminary paper<sup>12</sup> and shows that the decomposition is the result of an intramolecular oxidation-reduction in which the electrons migrate from the nitrogen to the methyl carbon atom, whereas the molecular rearrangement just discussed, which is also the result of an intramolecular oxidation-reduction reaction, involves a migration of electrons from the methyl carbon to the nitrogen, this course being the direct reverse of that followed in the thermal decomposition. The decomposition by heat and the rearrangement are therefore the results of two parallel and competing oxi-

<sup>10</sup> The interpretation is given by Stieglitz and Senior, Ref. 2 [THIS JOURNAL] p. 2729. Since this was written, Messrs. E. C. Gilbert and J. F. Smith in this Laboratory have effected the rearrangement of a number of hydrazine derivatives, including benzophenone-hydrazone. (May, 1922).—J. S.

<sup>11</sup> See Stieglitz and Leech, and Stieglitz and Stagner, Ref. 5.

<sup>12</sup> Ref. 2, (THIS JOURNAL p. 2731).

dation-reduction reactions of an intramolecular character. One of the main experimental difficulties encountered was the problem of reducing the loss of material by the thermal decomposition to a minimum. At best a yield corresponding to the rearrangement of somewhat more than a third of the substance was finally obtained.

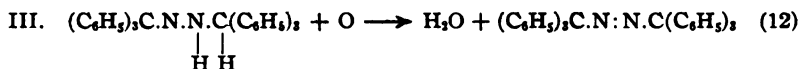
The next observations made were not anticipated and have raised new questions of interest. Among the reaction products *phenol* was obtained in appreciable quantities. It was at first thought that its presence might be due to some decomposition of the aniline group in phenylimido-benzophenone, the zinc chloride, when it is present in large excess, possibly reversing the well-known change of phenol into aniline by zinc-ammonium chloride.<sup>13</sup> Experiments made with phenylimido-benzophenone and zinc chloride proved that this is not the source of the phenol. Nothing was found in the literature indicating the formation of phenol from triphenyl-methylamine or its carbinol, from benzopinacone (Equation 6) or its decomposition product, benzohydrol. Furthermore, it was then found that when *bis*-triphenylmethylhydrazine is heated with zinc chloride *in the absence of air*, for instance in an atmosphere of carbon dioxide, no phenol is formed, but the formation of diphenyl is strongly suggested by its odor. The carrying out of the action in the presence of carbon dioxide in place of air led to the further unexpected observation that under these conditions there is *no rearrangement* to an aniline derivative; at most, small quantities of aniline were obtained in the working up of the products, which might be due to the presence of occluded air in the reagents used. These results open up a series of interesting questions, which can only be suggested here as the basis on which further investigation is being planned.

It is evident, in the first place, that the production of phenol is due to the oxidation of a phenyl radical at some stage of the action at the expense ultimately of the oxygen of the air. Two interesting possibilities suggest themselves. Phenol may be formed by the capture of oxygen by some of the phenyl radicals before they have reached their destination, the nitrogen atoms (see the middle phase of the action represented in Equation 10). Whether the phenyl radicals, originally positive, first capture some of the migrating electrons which lead to the rearrangement, and escape because they have become electrically neutral is a matter of fascinating speculation which can only be suggested here. In support of this conception we have the fact that the formation of *diphenyl* is indicated, as yet only by its odor, especially when oxygen is excluded. As far as we can discover, the formation of compounds of the type of phenol and diphenyl has never been observed before in the numberless rearrangements in which an aryl or an alkyl group migrates from carbon to nitrogen,

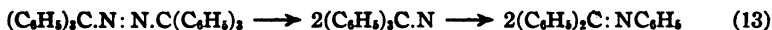
<sup>13</sup> Merz and Weith, *Ber.*, 13, 1299 (1880).

but none of these has been carried out, as far as we can find, at so high a temperature as 300°.

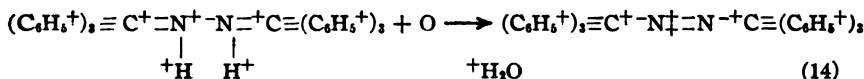
In the second place, Wieland<sup>14</sup> found that when azo-triphenylmethane is formed by oxidation of *bis*-triphenylmethylhydrazine, it decomposes at once, even at 0°, into triphenylmethyl: this compound is oxidized by air to its peroxide, which in turn is rearranged by heat into the diphenyl ether of benzopinacolone (Equation 4). This phenol derivative may be the source of the phenol obtained in our reaction. Wieland found, however, that the hydrazine is not oxidized to the azo compound by air, but requires more powerful oxidizing agents. It is possible, nevertheless, that at 300° a temperature never attained in Wieland's experiments, oxidation by air does occur. Furthermore, part of the azo compound might undergo the rearrangement leading to the formation of phenylimido-benzophenone, as follows.



and



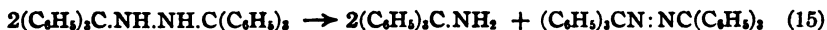
Electronically, we would have



Two electrons leave the nitrogen at the point indicated by the negative sign in heavy type, with the formation of water and azo-triphenylmethane. The dissociation of the latter into two molecules of triphenyl-methylimide  $(\text{C}_6\text{H}_5)_3\text{C.N}$ , needs no further explanation and the rearrangement of the imide would follow the course indicated in Equation 2 above.

No rearrangement of this kind was ever observed by Wieland in his attempts to prepare azo-triphenylmethane, and while the reaction which he did observe (decomposition into nitrogen and triphenylmethyl) was carried out in the cold (usually at 0°), a higher temperature would presumably simply accelerate this decomposition. Nevertheless, some of Wieland's work will be repeated as soon as circumstances permit, and efforts especially made to isolate azo-triphenylmethane in order that it may be subjected to sudden heating to 300°.

This interpretation still fails to account for the formation of the decomposition products of triphenyl-methylamine. To account for these we would have to assume that at 300° still another decomposition of the hydrazine occurs, never observed in its study, but analogous to the well-known decomposition of hydrazobenzene into aniline and azobenzene.



<sup>14</sup> Wieland, *Ber.*, **42**, 3020 (1909).

In that event, the azo compound must be formed and rearrangement should occur even in the absence of air, which does not seem to be the case.

If we assume, therefore, for the present simply as a working hypothesis that the course of the action is that given in Scheme I and that the formation of phenol is actually due to the oxidation of phenyl groups escaping rearrangement, then for every molecule of triphenyl-methylamine formed there should be produced either a molecule of phenylimido-benzophenone (Equations 1 and 2) or a molecule of phenol. The quantity of triphenyl-methylamine produced is found by the quantitative determination of its decomposition product, ammonia, and the quantity of phenylimido-benzophenone produced is found from a volumetric assay of the aniline formed by its hydrolysis. In addition, the quantity of phenol obtained was also determined volumetrically. Now, according to what has been developed above, the interpretation of the rearrangement outlined under I demands that the sum of the aniline and the phenol formed should be roughly of the order<sup>15</sup> of the amount of ammonia (triphenyl-methylamine) obtained. This result is well borne out by the experimental values as collected in Table II.

### Experimental Part<sup>16</sup>

I. Preparation of *sym.-bis*-Triphenylmethylhydrazine,  $(C_6H_5)_3CNH-NHC(C_6H_5)_3$ .—For the purpose of obtaining better yields, the compound was prepared by the treatment of triphenylmethyl bromide rather than of the corresponding chloride,<sup>17</sup> with hydrazine hydrate.

The triphenylmethyl bromide was prepared according to the method of Allen and Kölliker<sup>18</sup> and recrystallized from benzene. To the hydrazine hydrate (8 g.), covered with absolute ether (100 cc.), the triphenylmethyl bromide (27.4 g., 95% pure) was added in small portions throughout the course of about an hour, the mixture being constantly shaken. The reaction began immediately on the introduction of the bromide and proceeded at ordinary temperatures with evolution of heat and continuous precipitation of the *sym.-bis*-triphenylmethylhydrazine and hydrazine hydrobromide. The action was practically complete a short time after the last portion of triphenylmethyl bromide was added, but the reaction mixture was allowed to stand for a day to insure completion. The precipitate was collected on a filter and washed, in turn, with ether.

<sup>15</sup> Every molecule of triphenyl-methylamine formed gives a corresponding molecule of ammonia, our experiments having shown that the ammonia formation is practically quantitative when triphenyl-methylamine is heated with zinc chloride. But some of the phenyl groups may well escape combination with oxygen or with nitrogen. Thus, the formation of diphenyl was strongly indicated in the last experiment undertaken. The sum of the aniline and phenol formed should, therefore, be rather somewhat smaller than greater, than the amount of ammonia produced.

<sup>16</sup> I wish to use this opportunity to express my appreciation of the skilful and painstaking manner in which my young collaborator, Mr. Brown, has handled the rather complex experimental material which this problem has presented. All the experimental work was carried out by Mr. Brown.—J. S.

<sup>17</sup> Ref. 14, pp. 3021, 3025. Ref. 19, p. 2727.

<sup>18</sup> Allen and Kölliker, *Ann.*, **227**, 110 (1885).

alcohol, water, very dilute sodium hydroxide solution, water, alcohol and ether. The yield was 12.9 g. of crude material melting at 213°. Further purification by the method of Wieland gave 11.2 g. of the compound melting at 216°. A second recrystallization raised the melting point to 219–220°. Since decomposition takes place at the melting point, the melting-point tube containing the material was introduced into the temperature bath when it was 5° below the melting point of the compound.

## II. A Study of the Decomposition of *sym.-bis-Triphenylmethylhydrazine* at its Melting Point

The fact that the only evidences of a rearrangement had been obtained when the compound had been heated with zinc chloride at a temperature higher than that of its melting point, made a study of the melting-point decomposition imperative. At its melting point in air, *bis-triphenylmethylhydrazine* showed a marked evolution of gas and gave as a residue a dirty-white solid melting without purification at 85°. This residual solid mixed with triphenylmethane<sup>19</sup> melting at 92°, gave a melting point of 87°–90°. A sample of 1.5 g. of the *bis-triphenylmethylhydrazine* was then heated at 220–230° in an atmosphere of dry carbon dioxide until all evolution of gas ceased and the gas had been swept into a nitrometer filled with 50% potassium hydroxide solution. The residual material, while molten, was an amber colored liquid and in the solid state was a yellowish white substance.

The gas was examined first. It showed no loss of volume when passed through a palladium black tube, such as is used for determinations of hydrogen by absorption, nor when passed into potassium hydroxide, ammoniacal cuprous chloride and phosphorus pipets. This eliminates the possibility of hydrogen, unabsorbed carbon dioxide, carbon monoxide and oxygen being present. The gas was then mixed with several volumes of pure electrolytic hydrogen, and run into a eudiometer over mercury with a little conc. sulfuric acid on its surface. Continuous sparking across platinum electrodes within the tube produced a continuous reduction of volume and the deposition of a white solid on the acid-wet portion of the inner walls of the tube. In one experiment 0.7610 g. of *bis-triphenylhydrazine* gave 33.38 cc. of gas (0°, 760 mm.). The theoretical value for the evolution of all the nitrogen as N<sub>2</sub> is 33.02 cc. A portion of the gas (20 cc.) was mixed with pure hydrogen (67 cc.) and sparked until the acid threatened to touch the electrodes within the eudiometer. The residual volume was 10.2 cc. or 3.2 cc. over the 7 cc. excess of hydrogen added. The quantity 3.2 cc. is that portion of the original stoichiometric mixture of 80 cc. (20 cc. of N<sub>2</sub> + 60 cc. of H<sub>2</sub>) which had not reacted to form ammonia. This amount (3.2 cc.) is 4% of the original 80 cc. Now, the acid solution washed from the eudiometer and analyzed gave 0.0250 g. of ammonia. Twenty cc. of pure nitrogen, measured under the same

<sup>19</sup> Stieglitz and Senior, Ref. 2, p. 2732.

conditions as prevailed for the 20 cc. of gas which was mixed with hydrogen and sparked, would give 0.0261 g. of ammonia. The ammonia found (0.0250 g.) is thus 4.2% less than the theory demands, (0.0261 g.). Since the gas unconverted to ammonia is 4% of the original amount taken and the ammonia found is 4.2% less than theory demands for this same original amount of nitrogen and no other gases were found, the conclusion is drawn that the gas from the thermal decomposition of the hydrazine was all nitrogen.

The solid product of the decomposition of *bis*-triphenylmethylhydrazine appeared in part as a snow-white sublimate and in part as a residual solid in the bottom of the test-tube. Samples of sublimate were needle-like crystals and melted at 92°. When mixed with pure triphenylmethane<sup>18</sup> melting at 92° they melted at 92°. The identity of the sublimate is thus established. The remainder of the residual solid was crystallized from benzene and fused to free the crystals from the molecule of benzene present as benzene of crystallization. The product then melted at 92° and mixed with triphenylmethane melting at 92° gave a melting point of 91–92°. A sample of 0.7610 g. of *bis*-triphenylmethylhydrazine decomposed under the conditions previously stated, *i. e.*, in an atmosphere of carbon dioxide by heat in a bath at 220° to 230°, gave 0.6968 g. of residue in the test-tube and 0.0191 g. of sublimate which total 0.7159 g. The reaction equation calls for 0.7197 g. of triphenylmethane. Repeated tests for aniline and aniline derivatives in these residual solids were without exception negative.

These results indicate that *bis*-triphenylmethylhydrazine at its melting point decomposes practically quantitatively into nitrogen and triphenylmethane.

### III. A Series of Attempts to Secure Rearrangement of *sym.-bis*-Triphenylmethylhydrazine below its Melting Point or in Solution

In view of this decomposition at the melting point, an effort was made to secure rearrangement in solution or at temperatures below that at which the compound melted. Although the results were negative, the brief description of several may possibly save future repetition.

One-half g. of *bis*-triphenylmethylhydrazine was triturated with 8 g. of anhydrous zinc chloride and allowed to stand protected from moisture for 2 months at ordinary temperature. The mixture darkened during this time, but no trace of aniline could be detected when the mass was worked up and tested according to the method of Stieglitz and Senior.<sup>19</sup> Analogous samples which had stood for shorter lengths of time gave the same negative results.

One-half g. of *bis*-triphenylmethylhydrazine and 8 cc. of dry benzene were heated in a sealed tube at 250° for 30 minutes. The contents of the tube after cooling were found to be under marked pressure. The dark colored solution showed no traces of aniline derivatives but contained nearly pure triphenylmethane. The pressure in the

tube was then due to nitrogen, the same thermal decomposition having taken place as occurs when the solid compound is heated.

A sample of the hydrazine was heated with finely ground dry zinc chloride for 8 hours at 100°. During this time the yellow mixture went through a continuous color change and caked considerably. Although no gas evolution was visible, the residual hydrocarbons melted well below 100° indicating formation of triphenylmethane. No aniline could be found when the test previously referred to was applied.

The *bis*-triphenylmethylhydrazine with ground zinc chloride was heated at 170–180° for 3 hours. Slight evolution of gas could be detected and the mass softened. As before, no aniline could be detected. Triphenylmethane was identified as a product. This indicates that the thermal decomposition of the hydrazine can be secured at temperatures below its melting point by continued heating.

A mixture of *bis*-triphenylmethylhydrazine and zinc chloride was placed in dry benzene and boiled for 7 hours under a reflux condenser at the boiling point of benzene. The condenser had been thoroughly dried and was protected by a calcium chloride tube. Part of the yellow color of the mixture was taken up by the benzene. No aniline could be detected in the resulting solution or products. Triphenylcarbinol was identified as a product. It melted at 158–159°. Mixed with pure carbinol (m. p. 159–160°) it melted at 158–159°.

*Bis*-triphenylmethylhydrazine (0.065 g.) was mixed with phosphorus pentoxide and heated in a test-tube immersed in an acid bath at 105–110° until no further change in appearance was noticeable (about 2 hours). No aniline or aniline derivatives could be detected in the residue. A portion of the original compound was recovered unchanged.

A sample (0.062 g.) of the hydrazine was put into water (50 cc.) along with a trace of specially prepared platinum black,<sup>20</sup> and held at 50° for 30 hours. The mixture was acidified, heated, made alkaline and distilled with steam. No aniline could be detected in the distillate. The *bis*-triphenylmethylhydrazine was recovered unchanged.

A sample (0.09 g.) of the hydrazine, approximately 0.04 g. of the platinum black and water (20 cc.) were heated in a sealed tube at 170° for 1 hour. Tested as above, no aniline could be detected in the contents of the tube. The original compound was recovered unchanged.

Some of the hydrazine (0.5 g.) was heated with anhydrous aluminum chloride (5 g.) at 180° for 10 minutes. The hydrolyzed products gave no test for aniline. The products were not investigated further.

#### IV. A Series of Experiments to Determine Conditions for a Maximum Rearrangement by Zinc Chloride

Realizing that a continuance of the experiments to effect the rearrangement at temperatures below that of the melting point of the compound might result only in a vain search for a catalyzer, we decided to return to the original method of Stieglitz and Senior and to secure a greater degree of rearrangement, by a rigorous study of all the conditions involved, than had been obtained in this earlier work.

Accordingly, experiments were carried out under varying conditions and the degree of rearrangement was determined in each case by titration of the aniline recovered with 0.1 *N* sodium bromate solution.<sup>21</sup> In

<sup>20</sup> Loew, *Ber.*, 23, 289 (1891). Also see Tanatar, *Z. physik. chem.*, 40, 475 (1902) and 41, 37 (1902).

<sup>21</sup> Curme, *This Journal*, 35, 1162 (1913).



particular the temperature and the time of heating and especially, also, the shape of the vessel in which the reaction was carried out and the time required to heat the mixtures up to the reaction temperature were varied. The results are given in the table that follows. The significance of the first 8 columns is obvious. In the last column is given the result of heating phenylimido-benzophenone under the corresponding conditions with zinc chloride. The first 2 experiments (Nos. 12 and 17) were carried out in hard glass tubes, the next 4 in an Erlenmeyer flask of 60 cc. capacity on the floor of which the mixture was spread in a thin layer and in the last 4 experiments, for the securing of still more rapid heating, a 100cc. Erlenmeyer flask was used. A metal bath was employed and the temperature of the bath taken with the aid of a thermocouple. Since phenylimido-benzophenone,  $(C_6H_5)_2C=NC_6H_5$ , is probably the actual product formed by the rearrangement and the aniline is obtained by subsequent hydrolysis, parallel experiments under the same conditions were made with this product in order to determine whether it is destroyed by zinc chloride under the conditions of the experiment.

TABLE I  
DEGREE OF REARRANGEMENT BY ZINC CHLORIDE

Expt.	Sample G.	ZnCl <sub>2</sub> G.	Temp. °C.	Time Min.	Aniline		Aniline recovered from	
					Found G.	Calc. <sup>a</sup> G.	$(C_6H_5)_2C=N-C_6H_5$ % <sup>a</sup>	$C_6H_5NH_2$ %
12	0.50	5	300	10	0.005	0.09	6	78.5
17	0.50	5	330	5	0.015	0.09	16	90.4
19	0.61	6	330	3	0.024	0.11	22	..
21	0.59	6+	360	3	0.032	0.11	30	..
22	0.51	6+	400	3	0.030	0.09	32	..
23	0.52	7	390+	2	0.033	0.09	35	91.3
24	0.55	7	390+	4	0.031	0.10	31	} approxi- mately 90
25	0.51	7	390+	2	0.028	0.09	30	
28	0.78	7	450	1 <sup>3</sup> / <sub>4</sub>	0.038	0.14	27	
29	0.57	7	450	2	0.029	0.10	29	
30	0.57	7	450	1 <sup>1</sup> / <sub>6</sub>	0.035	0.10	34	}
32	0.52	7	450	1 <sup>1</sup> / <sub>6</sub>	0.031	0.09	33	

<sup>a</sup> These values are calculated on the basis of the assumption (Scheme I, p.1271 of the introduction) that each molecule of hydrazine yields one molecule of aniline and not two molecules (as demanded by Scheme II).

The method used in Expts. 30 and 32 was chosen as the best under the working conditions employed. Expt. 23 gave a better yield, but 60cc. flasks of the variety which after careful annealing would stand being plunged repeatedly into a metal bath at the temperatures used were not then immediately available.

The method employed in Expts. 30 and 32 was essentially this. The dry *bis*-triphenylmethylhydrazine was weighed into the specially dried

flask, the anhydrous zinc chloride finely ground in a hot dry mortar added to it and the two were thoroughly mixed. If the *bis*-triphenylmethylhydrazine is pure and both substances are thoroughly dry, little, if any yellow color appears when the two are mixed. The flask was fitted with an empty 30cm. calcium chloride tube and that closed with a short filled calcium chloride tube. The flask whose contents, protected from the moisture of the atmosphere, had thus been thoroughly mixed and shaken down into a thin layer over the bottom of the flask, was plunged into the molten metal bath at 450°. After 70 seconds it was removed and allowed to cool. The method for working up the product is essentially that described below (p. 1286) for the quantitative examination.

### Examination and Identification of the Products of Rearrangement

**Aniline.**—The identity of this compound was established by Senior<sup>19</sup> by the analysis of its chloroplatinate. Besides the observation of the characteristic purple color developed on the addition of calcium hypochlorite solution to the first drops of the steam distillate, the tribromo-aniline obtained from the titration of several of the acidified steam distillates containing aniline, was washed with water, and recrystallized from alcohol. This product melted at 118–119°. When mixed with tribromo-aniline, melting at 119–120°, it melted at 118–120°.

**Phenol.**—The quantitative preparation of phenol as tribromo-phenol is described below (p. 1286). The white precipitates from several titrations<sup>22</sup> were collected on a filter, washed with water and recrystallized from dilute alcohol. The fine, long, white needle crystals melted at 90°. Mixed with tribromo-phenol, melting at 94°, the product melted at 90–92°. The identity of phenol as a product of the reaction is thus established.

**Benzophenone.**—The quantitative separation of benzophenone in the form of its oxime is described below (p. 1286). Our qualitative work by similar methods yielded a considerable quantity of almost pure white crystals of benzophenone-oxime which, when dry, melted at 137–138°. Mixed with benzophenone-oxime melting at 141°, the substance melted at 138–139°. This established the presence of benzophenone among the hydrolyzed rearrangement products.

**Diphenylene-phenylmethane and Triphenylmethane.**—The hydrocarbons obtained (see below, p. 1286) melted at 82–83°. The melting point of this material<sup>19</sup> was not raised by further recrystallization from alcohol or benzene. However, in concentrated ether solution by a careful regulation of the rate of the spontaneous evaporation of the solvent, two distinct types of crystals were formed. One consisted of groups of fine needles growing from a common center; the other was made up of a relatively small number of large bar-like crystals. Both were colorless

<sup>22</sup> See Koppeschaar, *Z. anal. Chem.*, **25**, 162 (1886).

and the two were mechanically separated with ease. The first melted at 143–144° without purification. Recrystallization from alcohol gave it a constant melting point of 145–146°. Diphenylene-phenylmethane, prepared according to Kliegl<sup>23</sup> and freed from triphenylmethane, formed at the same time, and by repeated crystallization from alcohol, melted at 145–146°. An equal part mixture of the two compounds of this melting point melted at 145–146°. This established the identity of the diphenylene-phenylmethane produced in our reaction.

The larger crystals after being pressed between two filter papers melted at 92° without further purification. Mixed with triphenylmethane melting at 92°, they melted at 92° and hence were triphenylmethane.

**Triphenylmethane and Gum Resin.**—From the resins left by steam distillation, only triphenylmethane (m. p. 91°, identified as usual) was isolated.

#### V. The Decomposition of Triphenyl-methylamine at 450° in the Presence of Zinc Chloride and the Establishment of the Existence of Triphenyl-methylamine as an Intermediate Product in the Rearrangement of *sym.-bis*-Triphenylmethylhydrazine

Despite the thorough search made for triphenyl-methylamine and its hydrolytic product, triphenylcarbinol, among the rearrangement products, neither could be found. The properties of triphenyl-methylamine are such that quantities of it along with some triphenylcarbinol should have been found without difficulty, principally in the gummy residue of the steam distillation made in the determination of the aniline, if it were present in the melt resulting from the heating of *bis*-triphenylmethylhydrazine with zinc chloride to effect the rearrangement. Since none was found and its formation in the rearrangement was suggested by the theory under investigation, its decomposition by zinc chloride after its formation was indicated. Hence, it became essential to know the effect of heating triphenyl-methylamine with zinc chloride under conditions identical with those used to produce rearrangement of *bis*-triphenylmethylhydrazine. Accordingly, triphenyl-methylamine was prepared from triphenylmethyl bromide and dry ammonia.<sup>24</sup> To insure its being free from the hydrobromide, it was extracted in a Soxhlet apparatus with low-boiling ligroin.<sup>25</sup> It melted at 103° after crystallization from the ligroin. The following experiments were then carried out.

Triphenyl-methylamine (1.5 g.) was mixed with finely ground anhydrous zinc chloride (8 g.) and heated at 450° for 70 seconds, exactly as described in the previous section for the rearrangement of the *bis*-triphenylmethylhydrazine. The melt was treated with

<sup>23</sup> Kliegl, *Ber.*, 38, 287 (1905).

<sup>24</sup> Elbs, *ibid.*, 16, 1276 (1883).

<sup>25</sup> This method of purification of triphenyl-methylamine is due to Mr. H. C. Trimble of this Laboratory, whose dissertation is, as yet, unpublished.

ordinary ether and the resulting dark red solution was filtered from a dirty-white insoluble solid portion (A).

The solution was shaken with conc. sodium hydroxide solution, the ether portion separated, dried with anhydrous potassium carbonate and solid sodium hydroxide, and evaporated to dryness. The residue was dried *in vacuo* over solid potassium hydroxide. It was taken up in absolute ether and, because the solution was not quite complete, the ether extract was filtered. Dry hydrogen chloride, passed into the solution, gave a flocculent precipitate (B). The solution after filtration was partially decolorized with charcoal and evaporated to dryness. The residual gum was freed from ether *in vacuo* and dissolved in a little benzene. Crystallization took place rapidly. A portion of the crystals pressed between filter paper, fused on the steam-bath and allowed to solidify, melted at 90–91°. A mixture of this with triphenylmethane in equivalent quantities melted at 91–92°.

The insoluble material<sup>16</sup> (A) when covered with a little conc. sodium hydroxide solution and warmed gave copious quantities of ammonia. It evidently consisted of a zinc ammonium chloride.

The precipitate (B) was a clay colored, slimy material, which caked on the filter paper as it dried. It was very slightly soluble in alcohol and insoluble in water, in ether and in ligroin. It dissolved in chloroform and benzene, but crystallized from neither. On evaporation of these solvents both spontaneously and by heat no crystals could be obtained and the residue was a resin. When precipitated from either of these solvents by the addition of low-boiling ligroin, the substance was a clay colored, amorphous material. Examination under the microscope showed no crystalline material. It gave no test for chlorine or the chloride ion. Repeated treatment with conc. ammonium hydroxide produced no change in its properties. It possessed no melting point but darkened and shrank into a hard resin above 220°. Even at 290° no fusion had taken place. This cannot be the hydrochloride of unchanged triphenyl-methylamine.

In a further experiment the melts from two more samples of the fusion of triphenyl-methylamine with zinc chloride were washed into separate flasks, treated with alkali and distilled for ammonia in the usual way.

*Analyses.* Subs., (1) 0.5805, (2) 0.5402. Calc. for triphenyl-methylamine:  $\text{NH}_3$ , 0.0381,<sup>17</sup> 0.0355. Found: 0.0355, 0.0345.

The melt from a third sample was dissolved in ether and dil. hydrochloric acid. Each of the two solutions, after being well shaken and separated, was washed thoroughly with the other solvent. The portions of like solvents were combined. The aqueous portion containing the zinc chloride and the ammonia was rendered strongly alkaline and distilled for ammonia.

*Analysis.* Subs., (3) 0.5916. Calc.:  $\text{NH}_3$ , 0.0388. Found: 0.0384.

This result, in view of the separation of the ether and aqueous portions before distillation and the fact that no triphenylcarbinol was obtained from the distillation residue in (1) and (2), eliminates the possibility of any hydrolysis of unchanged triphenyl-methylamine in the first two determinations. Hence, we conclude that triphenyl-methylamine, when heated under the conditions previously stated, gives up its nitrogen as ammonia practically quantitatively.

In the distillate of Determinations 1 and 2 were small quantities of solid hydrocarbons which, on crystallization from the ether with which they were extracted, melted at 143–144°. Recrystallized from alcohol and mixed with diphenylene-phenylmethane

<sup>16</sup> The exact nature of this zinc chloride ammonia complex was not investigated.

<sup>17</sup> This value was calculated on the basis of one molecule of  $\text{NH}_3$  for one molecule of triphenyl-methylamine.

melting at 145°, it gave a melting point of 142–143°. Diphenylene-phenylmethane is thus identified as one of the products of decomposition.

As in the other experiment the residue from the ammonia Distillations 1 and 2 and the ether solution of 3 yielded triphenylmethane and gum or resin.

A sample of triphenyl-methylamine heated alone at 450°, as before, gave a strong odor of ammonia and a residue of triphenylmethane, diphenylene-phenylmethane and resin. This decomposition is entirely analogous to the thermal decomposition of triphenylmethyl bromide and triphenylmethyl chloride in which, respectively, hydrogen bromide and hydrogen chloride together with triphenylmethane, diphenylene-phenylmethane and resin are obtained;<sup>28</sup> and the decomposition with zinc chloride present is not unlike the decomposition of triphenylcarbinol when heated with solid phosphoric acid,<sup>22</sup> except that, in the latter case, water is removed instead of ammonia, the quantity of diphenylene-phenylmethane formed is much greater and the quantity of resin is very small.

In a further experiment a sample of triphenyl-methylamine (0.204 g.) with zinc chloride (8 g.) was heated as before at 450° for 70 seconds. The melt was dissolved in ether and hydrochloric acid, and the ether portion was separated and shaken with 20 cc. of 2 *N* sodium hydroxide solution. The alkali extract was rendered acid and distilled with steam. The first portion (1 cc.) was divided into three parts and tested for phenol as follows: (1) by the addition of ferric chloride; (2) by the addition of Millon's reagent and then nitric acid;<sup>29</sup> (3) by boiling with dil. nitric acid which will reveal traces of phenol by the odor of *o*-nitro-phenol in the hot solution. All tests failed to detect any phenol. A parallel experiment with phenylimido-benzophenone (0.220 g.) yielded negative results in all three tests.

All the decomposition products of triphenyl-methylamine had been recovered from the melt of *bis*-triphenylmethylhydrazine and identified as such except ammonia. *Bis*-triphenylmethylhydrazine (0.901 g.) and finely ground dry zinc chloride (10 to 11 g.) were therefore heated under the conditions and in the manner previously described for this compound. The melt was treated with ether and a small quantity of water. The aqueous portion when made strongly alkaline with concentrated sodium hydroxide and warmed, gave a strong odor of ammonia. The gaseous ammonia turned moistened red litmus paper blue and gave a heavy brown precipitate with Nessler's reagent.

Another sample of *bis*-triphenylmethylhydrazine (0.5 g.), without being mixed with zinc chloride, heated at 450° gave no detectable ammonia, neither was any aniline to be detected in the hydrolyzed products; while a sample (0.2295 g.) of phenylimido-benzophenone<sup>30</sup> heated in the same way gave 83% of the theoretical amount of aniline. The ether solution of the hydrocarbons from this heating of *bis*-triphenylmethylhydrazine, after decolorization with a little charcoal, yielded only triphenylmethane on complete evaporation. This melted at 90–91°. Apparently *bis*-triphenylmethylhydrazine does not rearrange when it is heated in the absence of zinc chloride, and ammonia is not produced when the rearrangement does not take place.

<sup>28</sup> Elbs, *Ber.*, 17, 701 (1884). Hemilian, *ibid.*, 7, 1208 (1874); *ibid.*, 11, 837 (1878). E. and O. Fischer *ibid.*, 11, 613 (1878); *Ann.*, 194, 257 (1878). Nef., *ibid.*, 309, 167 (1899). Schwarz, *Ber.*, 14, 1522 (1881).

<sup>29</sup> Almen, *Jahresber.*, 1878, 1079.

<sup>30</sup> This product was prepared by the reaction of Reddelieu, *Ber.*, 42, 4760 (1909), but purified as follows. At the end of the reaction, the melt was shaken with strong alkali, separated and distilled *in vacuo* to remove the excess of aniline. The well-cooled residue was freed from the remainder of the aniline on a cold porous plate and twice recrystallized from dil. alcohol. The product formed beautiful yellow flaky crystals, analyzing on hydrolysis for the calculated amount of aniline.

There can be little question but that triphenyl-methylamine was a primary product of the rearrangement and subsequently underwent the characteristic decomposition of that compound as outlined in the preceding paragraphs. This is established by the following facts holding for the conditions of the rearrangement of *bis*-triphenylmethylhydrazine: (1) triphenyl-methylamine gave practically a quantitative yield of ammonia; (2) benzophenone-phenylimide does not yield ammonia; (3) triphenyl-methylamine gave no hydrocarbon products not found among those of *bis*-triphenylmethylhydrazine; (4) *bis*-triphenylmethylhydrazine did not give ammonia when it did not undergo rearrangement and did give it when it did rearrange; (5) the molecular nitrogen and the triphenylmethane from the portion that underwent thermal decomposition and the phenol present could not give ammonia. Further evidence bearing out this conclusion is to be found in the quantitative study of the rearrangement products.

## VI. The Quantitative Study of the Rearrangement Products of *sym.-bis*-Triphenylmethylhydrazine

For a quantitative study of this rearrangement, approximately 15 g. of *bis*-triphenylmethylhydrazine was worked up in small portions. For the best yield of aniline under the conditions employed portions of about half a gram should have been used. Individual yields in this series (Table II) were sacrificed somewhat for total quantity of material worked up. Expts. 39 to 47 represent single samples, while in Expts. 47 to 51 two samples were heated separately and then combined for analysis in each experiment. The ratio of the hydrazine to zinc chloride was about 1:10. The preparation and heating of samples were as given in detail in the previous series of rearrangements.

After cooling the melt, it was treated with ordinary ether and a little dil. hydrochloric acid which took most of it into solution. The mixture was heated for several minutes under a reflux condenser to hydrolyze the phenylimido-benzophenone;<sup>31</sup> it was shaken thoroughly and, finally, the two solutions were separated carefully. The aqueous portion was extracted thrice with ether. Each of these ether extracts was washed with dil. acid. The original ether solution was washed twice with dil. acid. The acid portions were combined and likewise the ether portions and the combined portions filtered. This gave three products, (a) the acid portion, (b) the ether portion, and (c) the insoluble portion.

The acid portion (a) containing the ammonia, zinc chloride and the aniline formed by the hydrolyzed phenylimido-benzophenone was made strongly alkaline in a closed apparatus and distilled with steam into 20 cc. of 6 *N* sulfuric acid. The distillate (400 cc.) was extracted with alcohol-free ether to remove any hydrocarbons,<sup>32</sup> freed from any

<sup>31</sup> The completeness of this hydrolysis was tested in this way: 0.2297 g. of phenylimido-benzophenone was treated as indicated in the text and the aqueous portion treated for aniline. Calc. for aniline: 0.0831 g. Found: 0.0828 g.

<sup>32</sup> Despite the complete hydrolysis of the phenylimido-benzophenone and the thor-

dissolved ether and titrated for aniline with standard bromate solution. A slight excess of sodium thiosulfate was added and the tribromo-aniline removed by filtration. The filtrate was then made alkaline and the ammonia distilled in the usual manner. Cochineal was used as the indicator.<sup>33</sup>

The ethereal portion (b), containing the phenol, all the hydrocarbons and benzophenone, was shaken with sodium hydroxide solution (15 to 20 cc. of 2 *N*) and two like portions of water. The combined aqueous portions containing all the phenol<sup>34</sup> were rid of dissolved ether, made acid with hydrochloric acid and distilled with steam into dil. sodium hydroxide (5 cc.). The distillate (300 cc.) was rendered strongly acid and titrated with standard bromate solution for phenol.

The ethereal solution of hydrocarbons and benzophenone from the whole series or rearrangements was distilled nearly to dryness and distilled with steam until the distillate had entirely ceased to be milky in appearance. Solid hydrocarbons were still coming over but the benzophenone was practically all distilled.<sup>35</sup>

The recovery of benzophenone from the hydrocarbon mixture, extracted from the steam distillate, was carried out essentially as described earlier in this paper. The mother-liquor, after the removal of the benzophenone-oxime, was extracted and this extract, together with the mixture of hydrocarbons previously removed, was treated a second time for benzophenone. A very small second crop of the oxime was obtained.

The mixture of triphenylmethane and diphenylene-phenylmethane precipitated from the alkaline solution of benzophenone-oxime, after being washed free from alkali, melted at 80–84°. This was dissolved in a little ether and by a careful control of the concentration, two crops (1.10 g.) of triphenylmethane, m. p. 90°, were removed. The diphenylene-phenylmethane (0.05 g.) was then crystallized, and recrystallized from alcohol. It melted at 145–146°.

The residue from the distillation with steam was extracted with ether and the extract treated with animal charcoal, filtered, dried with calcium chloride, distilled to dryness and freed from ether *in vacuo*. Benzene was added to this residual gum and

ough extraction of the acid portion (a) with ether, there was some neutral product distilled at this point. This proved to be benzophenone melting at 45°. It was added to the ethereal portion (b). This suggests the probability of formation of a complex oxonium salt of benzophenone. The quantity of this material varied greatly. The controlling factors were not investigated but will be determined in this Laboratory. See Maass and McIntosh, *THIS JOURNAL*, 33, 71 (1911).

<sup>33</sup> The presence of the ammonium salt in no way affected the aniline titration. (See Kingscott and Knight, "Quantitative Organic Analyses," Longmans, Green and Co., 1914, p. 257; Sutton, "Volumetric Analyses," Blakiston's Son and Co., 1911, p. 387). The accuracy of the ammonia determination from the filtrate was sufficient for the purpose for which it was used. Some blank experiments gave these results: 0.0345 g. of aniline and 0.1164 g. of ammonium sulfate ( $\text{NH}_3$  content, 0.0300 g.) gave 0.0344 g. of aniline and 0.0303 g. of  $\text{NH}_3$ ; 0.0345 g. of aniline and 0.1164 g. of ammonium sulfate gave 0.0344 g. of aniline and 0.0301 g. of  $\text{NH}_3$ .

<sup>34</sup> The completeness of the separation, and the absence of condensation, of the aniline and the phenol on being heated with a concentrated solution of zinc chloride and hydrogen chloride were tested. A typical experiment gave these results: 0.0345 g. of aniline, 0.0305 g. of phenol and 0.0887 g. of ammonium sulfate ( $\text{NH}_3$  content 0.0229 g.) gave 0.0346 g. of aniline, 0.0304 g. of phenol and 0.0232 g. of ammonia.

<sup>35</sup> Benzophenone (0.70 g.) was distilled with steam, the condenser terminating in an adapter which dipped beneath the surface of the distillate as in the aniline, ammonia and phenol distillations. From the first 400 cc. of the distillate 0.672 g. of benzophenone was recovered by extraction.

from it two crops of triphenylmethane crystals, totaling 3.3 g., were obtained. The gum after removal of the crystals was again subjected to distillation with steam until 800 cc. of distillate had accumulated. This distillate on extraction yielded 0.2 g. of hydrocarbons, which were very largely diphenylene-phenylmethane (m. p. 144°). The small amount of contaminating material proved to be triphenylmethane. The residue from distillation with steam ( $\alpha$ ) was again extracted, dried *in vacuo* and treated with benzene in an effort to obtain further crystallization. The crystals formed were extremely small in amount and were not recovered.

The insoluble residue (c) left after treatment of the melt with ether and aqueous acid, was subjected, in the original filter papers, to extraction in a modified Soxhlet apparatus with chloroform as the solvent. This gave a carbonized residue ( $\beta$ ) and a chloroform solution of a resin-like material ( $\gamma$ ) in no way distinguishable from the precipitate (B) described in connection with the decomposition of triphenyl-methylamine, except that it was darker in color. This will be discussed later.

A portion (1.12 g.) of the benzophenone-oxime recovered was dissolved in alcohol, dil. hydrochloric acid added and the solution boiled for several hours; it was then diluted and extracted with ether. The dried extract yielded an oil which crystallized on being seeded with a crystal of benzophenone. This weighed 1.02 g. and melted at 45°. Recrystallized from ligroin it melted at 47.5° to 48°.

The identification of each of the compounds obtained was carried through again as follows.

## MELTING POINTS

Compound	Found °C.	Known compound °C.	Mixed sample °C.
Ammonia.....	.....	.....	.....
Tribromo-aniline.....	118-119	119-120	118-120
Tribromophenol.....	91-92	92-93	92-93
Benzophenone			
as oxime.....	139.5	141	140-141
as benzophenone.....	47.5-48	48	47
Triphenylmethane			
(from the steam distillate)...	90	92	90-91
(from the steam distillation residue).....	90-91	92	90-91
Diphenylene-phenylmethane.....	145-146	145-146	145-146

The gum or resin ( $\alpha$ ) residue from the distillation with steam and removal of triphenylmethane was apparently identical with that obtained in the decomposition of triphenyl-methylamine and as such was considered as a final product.

The residue ( $\beta$ ) from the chloroform extraction of insoluble portion (c) from the original melt was in no way distinguishable from carbon in its behavior in a flame and its total insolubility in benzene, a characteristic of free carbon.

As previously stated the residue ( $\gamma$ ) after evaporation of the chloroform was identical in every way but depth of color with the material obtained from the decomposition of triphenyl-methylamine. It showed the same solubilities and when precipitated from chloroform with low-boiling ligroin and dried, it gave the caked smear. Repeated precipitation failed to purify or change it. When heated in a melting-point tube, it darkened and shrank from 225-230° up (heated to 290°) but never melted so as to spread on or stick to the tube. After the heating, the material was shaken out of the tube and formed a hard, dark resin. It was probably a highly condensed or polymerized mass. A sample of the precipitated material finely ground was treated in aqueous suspension



with concentrated ammonium hydroxide. It underwent no change in appearance or the properties evidenced under heat and solvent. Treatment with other alkalis and acids did not affect it. These properties are not unlike those exhibited by the very highly polymerized products of the indene and cumarone series and other partly unsaturated bodies.

The quantitative determinations of the rearrangement products of this series are given in the table that follows. In this table, Part 1 gives the results for aniline, phenol and ammonia: Col. 1 gives the number of the experiment, Col. 2 the weight of samples used (given in values rounded to centigrams but calculated to milligrams), Col. 3 the aniline found, Col. 4 the yield of aniline expressed in percentages of the maximum calculated yield. In Col. 5 the weight of phenol is given and in Col. 6 the equivalent percentage of aniline, calculated on the assumption that each molecule of phenol represents a molecule of aniline lost in the rearrangement (see the introduction). In Col. 7 we have the sum of the aniline actually found and of the aniline equivalent of the phenol found. In Col. 8 the amount of ammonia found is given and in Col. 9 the percentage of the calculated yield found, figured on the basis of the assumption that each molecule of hydrazine gives by way of triphenyl-methylamine a molecule of ammonia. In Part 2, the results for benzophenone are summarized, the calculations being based on the 23.94% of rearranged substance shown by the aniline of the total of Col. 4 of the first part of the table. In Part 3 the yields of other products are given in grams.

TABLE II  
QUANTITATIVE DETERMINATION OF THE REARRANGEMENT PRODUCTS

1. Aniline, Ammonia and Phenol

1	2	3	4	5	6	7	8	9
No.	Sample G.	Aniline found G.	% of Calc.	Phenol found G.	An. eq. %	Sum of aniline and an. eq. %	Ammonia found G.	%
39	0.77	0.040	28.8	0.035	25.1	53.9	0.016	64.0
40	0.77	0.043	31.0	0.030	21.6	52.6	0.014	56.0
41	0.65	0.026	22.2	0.032	27.4	49.6	0.013	61.9
42	0.76	0.028	20.4	0.038	27.8	48.2	0.016	64.0
43	1.02	0.046	25.0	0.037	20.5	45.5	0.021	61.8
44	1.35	0.053	21.8	0.067	27.3	49.1	0.031	69.0
45	1.54	0.038	13.7	0.048	17.3	31.0	0.026	51.0
46	0.52	0.027	28.7	0.029	30.9	59.7	0.0115	67.6
47	1.61	0.071	24.5	0.067	22.7	47.2	0.0321	60.4
48	1.46	0.069	26.2	0.074	28.2	54.4	0.033	68.7
49	1.61	0.072	24.8	0.074	25.2	50.0	0.031	58.5
50	1.50	0.068	25.2	0.075	27.4	52.6	0.033	67.3
51	1.55	0.071	25.5	0.080	28.3	53.8	0.033	64.7
Total	15.11	0.652	23.94	0.686	24.94	48.9	0.3105	62.3

## 2. Benzophenone

Sample taken	Benzophenone-oxime		Benzophenone	
	Found	Calc.	Found	Calc.
15.12	1.22 <sup>36</sup>	1.38	1.12	1.27

## 3. Other Products

	From steam distillate	From steam distillate residue	Total
	G.	G.	
Triphenylmethane.....	1.10	3.30	4.40
Diphenylene-phenylmethane.....	.25	..	0.25
Gum resin-steam dist. residue.....	..	6.35	6.35
Carbonized residue ( $\beta$ ).....	..	..	0.30
Resinous material ( $\gamma$ ).....	..	..	0.35

VII. Rearrangements of *sym.-bis*-Triphenylmethylhydrazine in Other Atmospheres than Air<sup>37</sup>

With a view to the study of the rearrangement and the coincidental thermal decomposition by accounting for the whole of the nitrogen of the molecule in the products found, attempts were made to secure the rearrangement of the hydrazine in an atmosphere of carbon dioxide. It was expected that possibly a relation could be found between the percentage of the *bis*-triphenylmethylhydrazine that underwent the primary decomposition into nitrogen and triphenylmethane and the percentage of the *bis*-triphenylmethylhydrazine which underwent the rearrangement, and that by the measurement of the nitrogen evolved and the aniline produced at various temperatures, the extent of the thermal decomposition and of the rearrangement would be given. It was proposed to begin at temperatures below 300°, this being the only temperature at which, at that time, the arrangement had been effected.<sup>38</sup> Accordingly, the following experiments were carried out.

A sample (0.514 g.) of *bis*-triphenylmethylhydrazine was weighed into a hard glass tube, 5 g. of finely ground anhydrous zinc chloride added and the two intimately mixed. The tube was connected with a source of dry carbon dioxide and by an outlet to a nitrometer. When the apparatus had been freed from air, the tube was immersed in an oil-bath at 275° and retained there until nitrogen had ceased to be evolved. The nitrogen collected amounted to 3.7 cc. at 23° and 738.1 mm., uncorrected. The melt was dissolved out with ether and water, washed well with conc. sodium hydroxide solution,

<sup>36</sup> One g. of benzophenone and 2.3 g. of triphenylmethane yielded 0.95 g. of benzophenone-oxime and 2.27 g. of triphenylmethane when the mixture was treated as outlined in the text of this paper. Calc., 1.08 g. of the oxime. Hence  $1.22 + 0.13 = 1.35$  g. of the oxime calculated (1.38) in the text is accounted for.

<sup>37</sup> This work was done before the decomposition of triphenyl-methylamine was investigated and the presence of ammonia among these arrangement-decomposition products of *bis*-triphenylmethylhydrazine was discovered and its quantity taken as the measure of the minimum portion of the *bis*-triphenylmethylhydrazine which originally split into triphenyl-methylamine and the univalent nitrogen derivative, which rearranges to give phenylimido-benzophenone and phenol.

<sup>38</sup> By ourselves and by Stieglitz and Senior, Ref. 19, p. 2731.

hydrolyzed and distilled with steam after the addition of sodium hydroxide. No aniline could be detected in any portion of the distillate with calcium hypochlorite solution. The solid hydrocarbons in the distillate softened from 70° up and melted at 78–84°. Beyond this they were not investigated at this time.

A sample (0.664 g.) of *bis*-triphenylmethylhydrazine was treated as above except that a temperature of 300° was used. The evolution of the nitrogen seemed to be complete in about 3 minutes and it had all been swept over at the end of 10 minutes. The gas collected amounted to 6.8 cc., at 24° and 752.5 mm., uncorrected. As before, all efforts to detect aniline among the hydrolyzed products failed. The hydrocarbons extracted from the distillate with steam melted at 78–81° and, mixed with an equal quantity of triphenylmethane melting at 92°, melted at 85–88°. They were not further investigated.

After the rearrangement in air had been developed to give a yield of 35% of the calculated amount, the conditions of temperature, time, and container and methods of manipulation were applied to secure rearrangement in carbon dioxide. Four experiments were made. A mixture of 0.518 g. of *bis*-triphenylmethylhydrazine and 7 g. of zinc chloride prepared as described earlier in this paper was heated in an atmosphere of carbon dioxide, prepared by the heating of pure sodium hydrogen carbonate, and dried by being passed through 2 sulfuric acid wash-bottles. After the flask had cooled it was immersed in an ice-bath and the nitrogen swept into the nitrometer. The melt was lighter in color than those produced in air, being brown, and had no odor of phenol but one resembling that of *diphenyl*. It was dissolved in ether and water; the resulting solutions were shaken with conc. sodium hydroxide solution and the ethereal solution separated. To this ethereal extract, aqueous and ethereal solutions of hydrogen chloride were added, and the ether was distilled. The residue was warmed for 20 to 30 minutes on the water-bath, made alkaline and distilled with steam. No trace of aniline was found in the distillate. The hypochlorite test as applied easily detected 0.01 mg. of aniline in the same volume of solution.

The above experiment was repeated with 0.556 g. of *bis*-triphenylmethylhydrazine. Fifty cm. of tubing filled with glass beads covered with phosphorus pentoxide had been added to the drying system. The first few drops of the distillate gave a very faint coloration with the hypochlorite solution. The test was considered exceedingly doubtful.

The experiment was again repeated with 0.616 g. of *bis*-triphenylmethylhydrazine, the carbon dioxide being generated from pure magnesite. The first portion (1 cc.) of distillate in this case gave an appreciable color with hypochlorite solution. The color was not quite the characteristic purple but may have been affected by the opalescence of the distillate due to the hydrocarbons present.

One more experiment was made with 0.501 g. of the *bis*-triphenylmethylhydrazine. As in the last experiment, the first portion (1 cc.) of the distillate with steam gave a coloration with the hypochlorite solution.

In each of these experiments the first 400 cc. of the acid distillate with steam was extracted, freed from dissolved ether and titrated with standard bromate solution. Some bromate solution was used up and varied in amounts equivalent to 2 to 5 mg. of aniline. In no case, however, was there a precipitate of tribromo-aniline, while 3 mg. of aniline gives a marked precipitate of tribromo-aniline. Further, after extraction of the distillate in the fifth experiment, it was diluted to exactly 500 cc. and divided into two 250 cc. portions. One portion was rid of dissolved ether and then titrated with standard bromate solution. It required 0.71 cc. of the solution. The second portion (250 cc.) was made alkaline, extracted, freed from ether, acidified and titrated. This portion required 0.72 cc. of the bromate solution. The extract of the second portion, on being evaporated in a very slow stream of dry air, yielded no residue. The distillate of Expt. 4 was extracted 10 times with a total of 500 cc. of ether free from alcohol, and required

approximately the same quantity of bromate solution as the other distillates. After the standard solutions used in these titrations had been checked, and 0.0070 g. of aniline out of the 0.0101 g. theoretically possible had been recovered from 0.0279 g. of phenylimido-benzophenone on treatment identical with that applied to the *bis*-triphenylmethylhydrazine, it was concluded that if any phenylimido-benzophenone was formed by rearrangement in any of these experiments, it was exceedingly minute in amount. Traces of aniline, if proved, could be explained by the presence of the 0.4 to 0.5 cc. of air found to be occluded by the zinc chloride and freed when heated as described above.

The hydrocarbon extracted from the distillate with steam on evaporation of the ether proved to be triphenylmethane melting at 88–90°, while the steam distillation residue in benzene solution yielded triphenylmethane crystals which after being washed with ligroin melted at 88–89°.

The nitrogen evolved in these last four experiments varied from 50 to 75% of the total nitrogen in the sample taken.

Although *a priori* reasons make it unlikely that phenol was formed in these experiments (see the introduction), the alkaline sodium zincate solutions from the fourth, fifth and sixth experiments were saturated with carbon dioxide and extracted with ether. The extracts were allowed to evaporate spontaneously. The residues showed no test for phenol on the addition of ferric chloride.

These results, in the light of those from the rearrangements in air, raise the rather serious question as to whether the oxygen of the air is productive of the rearrangement or whether the carbon dioxide exerts an inhibitive influence on it. Qualitative and quantitative determinations of the ammonia in the products of the attempted rearrangements in carbon dioxide will show whether the carbon dioxide prevents completely the primary splitting into triphenyl-methylamine and the univalent nitrogen derivative which rearranges to give benzophenone-phenylimide, or only prevents this latter rearrangement after the splitting has occurred. If the splitting does occur, it is much less in carbon dioxide than in air, in view of the amounts of nitrogen and of the hydrocarbon products found. It is considered doubtful that the splitting occurs, but only experimental study which includes data on the amounts of ammonia formed can determine that. With data available on the rearrangement in an atmosphere of nitrogen or *in vacuo* a quantitative study of the ammonia, aniline and phenol as well as the other products from rearrangements effected in mixtures of oxygen and nitrogen, in which the percentage of oxygen is made to vary from zero to that of the air, should shed valuable light on the true part oxygen plays in the rearrangement.

Two arrangements, one in air and one in oxygen, carried out simultaneously in the same metal bath and with a 100cc. Erlenmeyer flask gave these results.

	Sample G.	ZnCl <sub>2</sub> G.	Temp. °C.	Time heated Sec.	Aniline found G.	Phenol found G.	Aniline calc. G.
Air.....	0.5192	7	450	70	0.0307	0.0279	0.0936
Oxygen.....	0.5701	7	450	70	0.0307	0.0318	0.1028

Because of difficulties in securing exactly duplicate physical conditions

conclusions cannot safely be drawn on less than a whole series of such measurements, together with the quantitative determinations of the ammonia produced in each arrangement.

### Summary

Our conclusions may be summarized as follows.

1. The formation of an aniline derivative by the rearrangement of *sym.-bis*-triphenylmethylhydrazine, as observed by Senior and the one of us, was fully confirmed.

2. Benzophenone was isolated as a product of the hydrolysis of the presumable primary rearrangement product phenylimido-benzophenone.

3. The decomposition products of triphenyl-methylamine, namely, ammonia and diphenylene-phenylmethane and triphenylmethane, which are formed when triphenyl-methylamine is heated with zinc chloride, were also found in quantity in the reaction products and the conclusion drawn that triphenyl-methylamine is a primary product of the action studied and is then decomposed in the manner indicated.

4. Triphenylmethane and nitrogen were proved to be products of the thermal decomposition of the hydrazine, the result of an intramolecular oxidation-reduction in a direction reverse to that which causes the rearrangement.

5. Phenol was obtained in quantity when the rearrangement reaction was carried out in air but none was found when the action was carried out in an atmosphere of carbon dioxide. The hypothesis has been tentatively formulated that the formation of phenol is due to the capture of oxygen by escaping migrating phenyl radicals.

6. In support of this view the sum of the aniline and the phenol obtained was found to be roughly equal to the total amount of ammonia formed.

7. The observation was made that there is apparently no rearrangement in the absence of air, a result which demands further investigation of the possibility that the rearrangement is the result of an oxidation reaction in which the oxygen of the air takes part.

8. The interpretation of the reactions from the point of view of the theory of electronic valences is given and accords well with the explanation of other rearrangements of this general type.

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[CONTRIBUTION FROM THE KENT CHEMICAL LABORATORY OF THE UNIVERSITY OF CHICAGO]

## THE ELECTRON THEORY OF VALENCE AS APPLIED TO ORGANIC COMPOUNDS

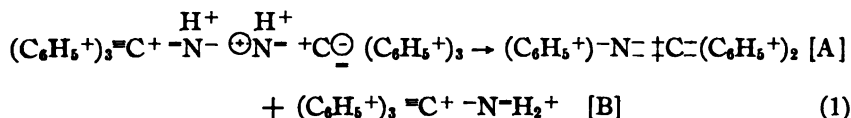
By JULIUS STIEGLITZ

Received September 7, 1921

Since the writing of the preceding article (1917) by R. L. Brown and myself on the molecular rearrangement of *sym. bis*-triphenylmethylhydrazine, considerable work has been done on the development of the electron theory of valence by G. N. Lewis, Langmuir, Kossel and W. A. Noyes, in addition to other authors. Of particular importance for our problem have been the opposing views as to the existence in organic compounds of "polar" valences or of "non-polar" valences, as defined by Lewis, by Bray and Branch<sup>1</sup> and by J. J. Thomson.<sup>2</sup> In the article by Brown and myself the conception of definite positive and negative charges on carbon, hydrogen, nitrogen and oxygen atoms in organic compounds has been used as in previous discussions of molecular rearrangements from this laboratory.<sup>3</sup>

In this article it is proposed to consider critically the value of the two theories, polar and non-polar, in the interpretation of the rearrangement of *bis*-triphenylmethylhydrazine and related compounds, as well as in following other types of reactions in organic chemistry, in which the writer has been actively interested.

I. From the point of view of polar valences the molecular rearrangement of the hydrazine would proceed as follows.



The final products are phenylimido-benzophenone (A) and triphenyl-methylamine (B). In this interpretation the source of instability or the "fault" in the original molecule is the nitrogen atom  $^+\text{N}^-$  which needs 2 electrons in order to go over into its most stable form  $\text{N}^=$  as in ammonia. Whatever the mechanism of the rearrangement is, this nitrogen atom is *ultimately* found as  $\text{N}^=$  in triphenyl-methylamine (B) or in phenylimido-benzophenone (A). We have assumed as the most direct and simplest course that the "slip" starts with the capture of 2 electrons by  $^+\text{N}^-$  from the neighboring carbon atom (the encircled charges  $\oplus$  and  $\ominus$  indicate the course of the slide of electrons), which necessitates the loss of a phenyl

<sup>1</sup> Bray and Branch, *THIS JOURNAL*, **35**, 1440 (1913). G. N. Lewis, *ibid.*, p. 1448; **38**, 762 (1916).

<sup>2</sup> Thomson, *Phil. Mag.*, **27**, 757 (1914).

<sup>3</sup> See literature references in *Proc. Nat. Acad. Sci.*, **1**, 196 (1915) and *THIS JOURNAL*, **36**, 272 (1914), **38**, 2046 (1916), where references to previous articles are given. See also L. W. Jones, *Am. Chem. J.*, **50**, 440 (1913), etc.

group ( $\text{C}_6\text{H}_5^+$ ) by the new positive corner of the methyl carbon atom and the capture of the phenyl group by the new negative charge on the nitrogen atom. It might well be possible that the slip starts with the capture of 2 electrons by  $^+\text{N}^-$  from the neighboring *nitrogen* atom, leaving an unstable univalent nitrogen derivative  $(\text{C}_6\text{H}_5^+)_2\equiv\text{C}^+-\text{N}$  which then rearranges as the result of the recapture of the lost electrons by the nitrogen atom from the neighboring carbon atom, phenylimido-benzophenone (B) resulting.<sup>4</sup>

In this interpretation two definite relations stand out. Without any *ad hoc* assumptions, we have, at first, an obvious *cause* for the molecular rearrangement in the unquestioned instability of  $^+\text{N}^-$ , containing only 6 valence electrons, as compared with  $\text{N}^-$  in which the full complement of 8 electrons is found in the valence electron shell of the nitrogen atom. In the second place, in the rearrangement the one methyl carbon atom is very evidently *oxidized* by the loss of 2 electrons to the nitrogen. As a matter of fact in the reaction products phenylimido-benzophenone (A) is a derivative of a ketone, benzophenone  $(\text{C}_6\text{H}_5)_2\text{C}\ddagger=\text{O}$ , which it forms by hydrolysis, while the original compound is a derivative of an alcohol, triphenylcarbinol  $(\text{C}_6\text{H}_5)_3\text{C}^+-\text{OH}$ , and is indeed prepared from triphenylmethyl chloride  $(\text{C}_6\text{H}_5)_3\text{C}^+-\text{Cl}$ .

These two advantages—they are fundamental—are not found in the interpretation on the basis of the non-polar valence theory which follows.

II. Of the various theories of non-polar valence brought forward the author would incline to the type of non-polar valence first presented by Bohr<sup>5</sup> and to the somewhat similar views of G. N. Lewis.<sup>6</sup> We have Bohr's well-known conception of the hydrogen molecule as consisting of 2 positive atoms held together by 2 common electrons rotating in an orbit in a plane between the two atoms, which we may express as  $\oplus : \oplus$ . G. N. Lewis's views postulate a similar pair of electrons, but apparently these do not rotate (*i. e.*, they are essentially in fixed positions). Kossel<sup>7</sup> has applied similar views to other molecules, and the views of Lewis and Langmuir, as far as our present discussion is concerned, may be considered to express essentially the same fundamental conception. A pair of such binding electrons would be found, for instance, at each of the 4 valence positions, *i. e.*, the 4 tetrahedral corners of the Le Bel-van't Hoff carbon atom.<sup>8</sup>

Representing, as Lewis does, two such binding electrons by the symbol : we may also represent bis-triphenylmethylhydrazine as

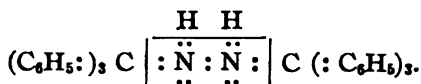
<sup>4</sup> See Stieglitz and collaborators, Ref. 3.

<sup>5</sup> Bohr, *Phil. Mag.*, 26, 476, 857 (1913). See p. 874 in regard to the application of this conception to carbon valences.

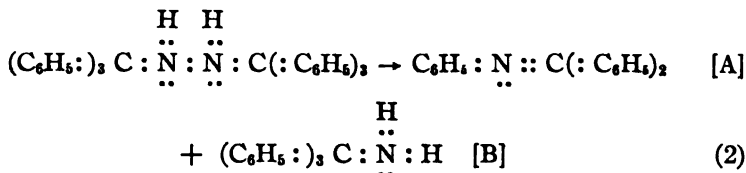
<sup>6</sup> Lewis, *THIS JOURNAL*, 38, 762 (1916).

<sup>7</sup> Kossel, *Ann. Physik*, 49, 229 (1916).

<sup>8</sup> Ref. 5, p. 874. Ref. 6, p. 780.



The following equation would express the rearrangement.



An ammonio-nitrogen atom of the type found in ammonia and the amines has either 3 extra electrons as expressed in  $\text{N}=(^+\text{H})_3$  or there are 6 non-polar electrons binding the nitrogen to hydrogen and 2 non-active valence electrons as expressed by  $\text{H}:\ddot{\text{N}}:\text{H}$ . In either event, the valence shell

would contain the octet of electrons, which represents a condition of stability. Now, in the hydrazine each nitrogen atom has its full octet of electrons as is seen in the above formula, and without some further assumption it is not at all evident why the molecule should be unstable and why it should undergo a rearrangement. It is true that the pair of nitrogen atoms, *if separated*, between them can contain 16 valence electrons whereas they hold jointly only 14 in the hydrazine, but individually each atom already has its full complement in the hydrazine and should be stable. In the rearrangement 2 electrons are supplied to the nitrogen by the migration of  $\text{:C}_6\text{H}_5$  from a methyl carbon atom to one of the nitrogen atoms and we ultimately have the separate nitrogen atoms with the maximum number (16) of electrons, but from the valence theory alone it is not at all evident why the separated nitrogen atoms should represent a condition of greater stability.

Further, each of the methyl carbon atoms has its octet of valence electrons both before and after the rearrangement and it is not at all apparent, without further assumptions, that one of them has actually been *oxidized* (lost electrons) to form a derivative of benzophenone rather than of triphenylcarbinol.

It is quite evident that in these two respects of fundamental importance, in showing the source of the instability of the hydrazine and in expressing the intramolecular oxidation and reduction characteristic of the rearrangement, the polar valence theory is unqualifiedly superior, in the interpretation of the rearrangement, to the non-polar valence theory.

Similar relations could be used to express the molecular rearrangements of other compounds of this class, which have been studied in this laboratory, the halogen-amides, the hydroxylamine derivatives, the azides, the per-



oxides, etc. The interpretation from the point of view of polar valences would in every instance without any specific assumptions show that the cause of the rearrangement is to be found in an unstable atom ( $\text{Cl}^+$ ,  $\text{Br}^+$ ,  $\text{O}^+$ , etc.) which represents a fault and which by depriving some other atom of electrons in order to go over into the stable forms ( $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{O}^-$ ) brings about as a sequel the shifting of groups. The interpretation with the aid of the non-polar valence theory would not reveal any fault in the molecules and would not express the net result of oxidation of some atom, by reduction of some other atom, which is an experimental fact of importance. It will not be necessary to discuss these other rearrangements in detail because the line of argument would follow closely that used in the above discussion.

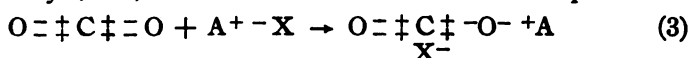
It is evident that while we can express the fundamental relations mechanically and arithmetically in the above reactions from the point of view either of polar or of non-polar valences as found in organic molecules, the question which must interest us most profoundly, namely, which method of expression represents better true relations, has been answered unequivocally in favor of the polar valence theory. In connection with still other fundamental reactions of organic chemistry, the writer wishes to explain here, as briefly and succinctly as possible, why he believes that the polar valence theory, as used originally by J. J. Thomson and later by Falk and Nelson, Jones, Fry, W. A. Noyes, the author himself and others,<sup>9</sup> gives a better representation of the facts of organic chemistry than the non-polar valence theory. It is to be explicitly understood, however, that this polarity is perhaps of a quite different order from the extreme polarity of an electrolyte such as sodium chloride.<sup>10</sup> Wherein the difference lies is a problem of atomistics and the writer himself does not care to advance any theory as to the difference. The insistence here is made on polarity as expressing a definite difference in electric charge between two linked atoms, one behaving as a positive, the other as a negative atom.

One will find such evidence in favor of polarity in numberless reactions which show the presence of unquestionable *directing forces*, which follow quite naturally from the polar valence forces without any further assumptions whatsoever, and for which the non-polar forces would demand some further specific interpretative assumptions. One might be inclined to consider whether the *reacting molecules* are the polar ones in these reactions—which unquestionably is the case—and whether the preponderating

<sup>9</sup> References are given in *Proc. Nat. Acad. Sci.*, Ref. 3.

<sup>10</sup> Cf. Lewis, Ref. 6. The writer's views approach those of this brilliant author except that for the reasons given in this article he cannot accept the view of actual, complete non-polarity, not to speak of a reversal of polarity (e. g.,  $\text{C}^{++++}\text{H}^{-}$ , Ref. 6, p. 182) and would emphasize the polarity of organic compounds, and the value of the conception in organic chemistry. In the interpretation of oxidation and reduction, the view of completely *polar* structures has very decided advantages [See below, and cf. Falk and Nelson, *THIS JOURNAL*, 36, 209 (1916)].

mass of molecules are non-polar and inert, existing in equilibrium with the reacting polar molecules just as the ions, say, of acetic acid are in equilibrium with the large proportion of non-ionized acetic acid. That is a question indeed for physical investigation and its solution might bridge the gap between the opposing views. The impressive fact remains that most of the reactions that follow always go in only one way, and never in any other (cases when the directive forces act in two ways will be explicitly discussed). For instance, carbon dioxide, for which Thomson assumes non-polar structure, always absorbs reagents such as water, ammonia, metal alkyls, etc., in accordance with the well-known equation.



the positive component,  $\text{H}^+$ ,  $\text{Zn}^{++}$ ,  $\text{Na}^+$ ,  $\text{Mg}^{++}$ , etc., invariably going to the negative oxygen, the negative component  $\text{X}^-$  invariably going to the positive carbon. For a non-polar union  $\text{O}::\text{C}::\text{O}$  one would imagine that the planes of the orbits or positions of the electrons through collisions with other molecules and the vibrations of the atoms, would move<sup>11</sup> either closer to oxygen, leading to the polar structure  $\text{O}=\ddot{\text{C}}\overset{\text{O}}{\vdots}\text{O}$  (D) or closer to the carbon, leading to  $\text{O}\overset{\text{O}}{\vdots}\text{C}=\ddot{\text{O}}$  (E). In fact the breakdown of carbon dioxide under the bombardment of positive rays apparently according to both D and E, first led Thomson to consider carbon dioxide to be non-polar and to revise his earlier views of polar structure. But the chemical fact remains that *all* of the absorption reactions of carbon dioxide proceed strictly according to Equation 3 and never by the remotest chance do we seem to get a compound  $\text{O}=\text{C}-\text{OX}$  such as  $\text{O}=\text{C}-\text{OCH}_3$ , or  $\text{O}=\text{C}-\text{OCH}_3$ ,



a formate, by the action of sodium methide or zinc methide<sup>12</sup> on carbon dioxide. The formates are quite stable compounds and are obtained easily by absorption reactions of carbon monoxide through the latent valences of the bivalent carbon atom.

The same *one-sided* absorption is always shown by all  $>\text{C}\overset{\text{O}}{\vdots}\text{O}$ ,  $>\text{C}\overset{\text{S}}{\vdots}\text{S}$ ,  $>\text{C}\overset{\text{N}}{\vdots}\text{N}^-$  etc. derivatives (aldehydes, ketones, esters, etc.) unless we deliberately first reduce the carbon atoms to the corresponding alcohols etc., by means of electrons from nascent hydrogen or some metal, from an electric current or some similar source.

### Absorption by Olefins<sup>13</sup>

An illuminating behavior, in connection with the problem of polar *versus* non-polar valences, is shown in the absorption relations of such an

<sup>11</sup> Cf. Lewis, Ref. 6, p. 782.

<sup>12</sup> Stieglitz, "Qualitative Analysis," Century Co., 1912, Vol. I, p. 177. L. W. Jones, Ref. 3, p. 420.

<sup>13</sup> The views here presented were expressed by the author in addresses given at Johns Hopkins University and as retiring Vice-President of the Chemistry Division of

olefin as propylene. It behaves exactly as if by far the greater proportion of propylene or the by far more active part<sup>14</sup> has the definite polar structure

$$\begin{array}{c} \text{H} \quad \text{H} \\ \text{H}_3\text{C}-\text{C}^{\dagger}=\text{CH} \end{array} \quad [\text{A}] \quad (\text{only the essential valences are indicated}),$$
 perhaps in equilibrium<sup>1</sup> with a small fraction, or a sluggishly reacting fraction,

$$\begin{array}{c} \text{H} \quad \text{H} \quad \quad \text{H} \quad \text{H} \\ \text{H}_3\text{C}=\text{C}^{\dagger}\text{CH}[\text{B}] \text{ or } \text{H}_3\text{C}.\text{C}^{\dagger}\text{CH}[\text{C}] \end{array}$$
 of the electromeric substance  $\text{CH}_3\text{C}=\text{C}^{\dagger}\text{CH}[\text{B}]$  or  $\text{H}_3\text{C}.\text{C}^{\dagger}\text{CH}[\text{C}]$ . The absorption of acids like hydrogen chloride, hydrogen bromide, etc., leads almost (but not quite<sup>15</sup>) exclusively to *iso*-propyl derivatives such as  $(\text{CH}_3)_2\text{CHCl}$ ;<sup>16</sup> the absorption of hypochlorous acid,  $\text{HOCl}$ , on the other hand, carries the *positive* chlorine<sup>16</sup> to the outside carbon atom, and  $\text{CH}_3\text{CHOHCH}_2\text{Cl}$  is formed.<sup>17</sup> Similar relations hold for the absorption by cinnamic acid, which lead to the formula  $\text{C}_6\text{H}_5.\text{HC}^{\dagger}=\text{CH}.\text{COOH}$ .

The small quantity of *normal* propyl chloride  $\text{CH}_3\text{CH}_2\text{CH}_2\text{Cl}$  observed by Michael is best understood as indicating the presence of a small proportion of the electromer B, or possibly even C, as there is not the slightest indication of any electromeric equilibrium  $\text{H}^+\text{Cl}^- \rightleftharpoons \text{H}-\text{Cl}^+$ . On the other hand, for such compounds as bromine chloride, bromine iodide, etc., we have every reason to consider that we must have equilibria, such as between bromine chloride and chlorine bromide  $\text{Br}^+\text{Cl}^- \rightleftharpoons \text{Cl}^+\text{Br}^-$  (as well as  $\text{Br}:\text{Cl}$ ) since both halogens have a very strong affinity for electrons, which must lead to an equilibrium condition.<sup>18</sup> As a matter of fact, we do get notable mixtures of such isomers as  $\text{CH}_3\text{CHCl}.\text{CH}_2\text{Br}$  and  $\text{CH}_3\text{CHBr}.\text{CH}_2\text{Cl}$  in such fair proportions as would be favored by the above equilibrium relation.<sup>19</sup>

the American Association for the Advancement of Science at Pittsburgh in 1917. Since then E. J. Cuy has published an excellent discussion of electron valences in carbon chains, which includes some of these relations [THIS JOURNAL, 42, 503 (1920)]. Nelson and Falk discussed the same in 1910 (*ibid.*, 32, 164) but the present writer's conclusions differ in some essential respects from those of these authors.

<sup>14</sup> There are of course, always two kinds of factors involved in the formation of definite products, mass action and velocity coefficients of reaction.

<sup>15</sup> The observation that a little propyl chloride is formed in the absorption of hydrogen chloride is the basis of this conclusion. See A. Michael, *J. prakt. Chem.*, 60, 286, 409 (1899) and Falk and Nelson, Ref. 13.

<sup>16</sup> Stieglitz, THIS JOURNAL, 23, 796 (1901).

<sup>17</sup> When  $\text{Cl}^+$  and  $\text{Br}^+$  enter into combination with  $\text{C}^-$ , the combination is commonly followed by intramolecular oxidation and reduction to  $\text{C}^+\text{Cl}^-$ ,  $\text{C}^+\text{Br}^-$ . Positive iodine has been recognized by Jones in one of the 4 iodine atoms in carbon tetra-iodide and Howell and Noyes [THIS JOURNAL, 42, 99 (1920)] have found it in iodo-acetylene. Fry. [*ibid.*, 38, 1328 (1916)] and Nicolet [*ibid.*, 43, 2081 (1921)] have found evidence of positive halogen in certain benzene derivatives.

<sup>18</sup> Cf. Lewis, Ref. 6. Experimental work in the study of these equilibria has been started by A. T. McPherson in this laboratory.

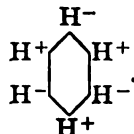
<sup>19</sup> Michael, Ref. 15. Falk and Nelson seem to give propylene the structure [C] as the preferable structure on the basis of the character of these absorption products

The relatively inert element carbon seems to have no such outweighing preference either for negative charges (gain of electrons) as exists for chlorine and bromine or for positive charges (loss of electrons) as exhibited by metals, or sulfur and phosphorus, etc. Consequently it is to be considered that particular conditions, such as the presence of specific catalysts, may cause a shift of the valence electrons between carbon atoms (oxidation and reduction) and lead to derivatives of electromers, since we must conclude that such molecules will be rather sensitive to the net effect of the forces in the whole molecule, far more so than is the case with such extreme atoms as chlorine, bromine, sulfur, phosphorus, etc. Emphasis should be placed in a study of this character rather on simple, direct actions taking place under ordinary conditions.

### The Crum Brown-Gibson Rule and the Structure of Benzene<sup>20</sup>

In the Crum Brown-Gibson<sup>21</sup> rule of substitution in the formation of benzene derivatives we have further most important evidence of the existence of powerful directing forces in organic compounds, which result in the ready formation of definite derivatives and automatically prevent the formation of isomers. Thus, as is well known, phenol reacts in the *ortho-ortho-para* positions, and nitrobenzene, benzoic acid, etc., in the *meta* positions. To Fry<sup>22</sup> belongs the credit of the first attempt to explain these relations with the aid of definite concepts of the electron theory of valence. But Fry's interpretation involves the assumption of the presence of nega-

tive hydrogen atoms in benzene, as expressed in the formula



It is further assumed that only the positive hydrogen atoms react with such reagents as chlorine ( $\text{Cl}^-\text{Cl}^+$ ), bromine, nitric acid, etc. Now, a negative hydrogen atom must be a powerful reducing atom, since without question the most stable form of hydrogen is  $\text{H}^+$ , and indeed metallic hydrides  $\text{Na}^+\text{H}^-$ ,  $\text{Ca}^+(\text{H}^-)_2$ , etc., whose electrical structure follows from their ready hydrolysis to metallic hydroxide and hydrogen,<sup>23</sup> easily catch fire in (Ref. 13, p. 1643). If that were the structure, hydrogen chloride and hypochlorous acid should yield large proportions of the isomeric absorption products. Such is not the case.

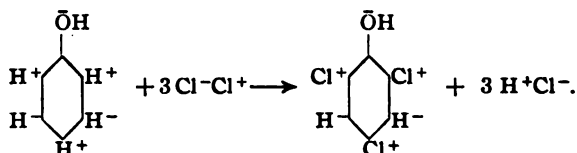
<sup>20</sup> This part of the report was presented before the Chemistry Division of the Pacific Coast Division of the American Association for the Advancement of Science at Berkeley, on August 5, 1921. See also Kharasch and Chalkley, *THIS JOURNAL*, 43, 608 (1921).

<sup>21</sup> *J. Chem. Soc.*, 61, 366 (1892).

<sup>22</sup> Fry, *Z. physik. Chem.*, 76, 385 (1911). Presented before the Cincinnati Section of the American Chemical Society in January, 1908.

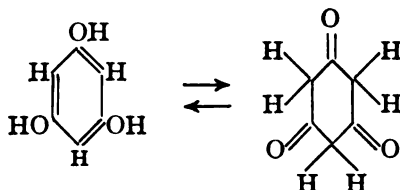
<sup>23</sup> Lewis and Bardwell have confirmed this conclusion by the electrolysis of sodium hydride (private communication).

the air as a result of the tendency of  $H^-$  to transfer its extra electrons to the oxygen of the atmosphere. No doubt the ionization of metallic hydrides brings out the maximum reducing power of negative hydrogen, but it would be illogical to consider that we have negative hydrogen in benzene without a trace of evidence of its presence,<sup>24</sup> shown in reducing power or instability. Benzene is eminently resistant to oxidation and extraordinarily stable. Furthermore, in the reaction of chlorine on benzene derivatives we are asked to believe that the reactive positive chlorine atoms, with an extraordinary tendency to absorb electrons, do not react with the negative hydrogen atoms, with their great tendency to release their extra electrons, for Fry's theory formulates the reaction between chlorine and phenol, for instance, as proceeding in the following way in order to account for the substitution in *ortho-ortho-para* positions:



Finally, we have as yet no competent evidence of negative hydrogen attached to carbon in any other type of organic compound.

There is, however, an electrical basis for the Brown-Gibson rule of substitution which may be developed by the application to benzene derivatives of facts determined experimentally in the simple field of the aliphatic series of organic compounds and without a single *ad hoc* or specifically new assumption. The development of this interpretation<sup>25</sup> may well start with a consideration of the behavior of phenols. Phenols are in every respect the aromatic analogs of aceto-acetic ester:<sup>26</sup> they form the same type of deeply colored ferric salts; they form enol-keto tautomers, as is most clearly illustrated by the behavior of phloroglucinol



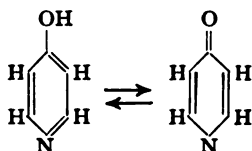
<sup>24</sup> Comparable with the ready evidence of the presence of positive chlorine, bromine, iodine, etc. (see below).

<sup>25</sup> Cf. Falk and Nelson, *School of Mines Quarterly*, 30, 187 (1909), *THIS JOURNAL*, 32, 1644 (1910), 33, 1150 (1911); etc. See also Vorländer, *Ber.*, 52, 263 (1919). Kharasch, Ref. 20.

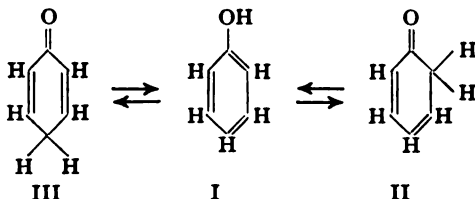
<sup>26</sup> K. Meyer, *Ann.*, 398, 51, 80 (1913). Meyer's views do not include any considerations of electrical valence forces.

about whose structure as a triphenol or triketone the usual controversy is to be found in the literature, resulting from the tautomeric behavior of the compound. For instance, phloroglucinol is soluble in alkali and forms ethers and esters—phenol characteristics—and it also forms a tri-oxime, a ketonic reaction. The alkali salts of phloroglucinol as well as of resorcinol when treated with ethyl iodide may be alkylated in such a way as to give  $(C_2H_5)_2C-C=O$  derivatives,<sup>27</sup> the alkylation affecting the  $-CH_2-$  group between the carbonyl groups in the way that is so well known for the alkylation of aceto-acetic ester.

A minor point of difference between phenol and aceto-acetic ester is that it no doubt forms *para* as well as *ortho* tautomeric ketones, exactly as oxypyridine is known to form the pyridone tautomer,

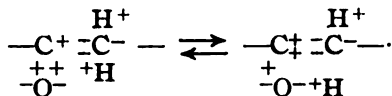


We have then for phenol the system<sup>28</sup>



in which Structure I presumably is by far the most stable.

Now, the formation of ketonic tautomers by phenol, resorcinol, phloroglucinol, etc., means that the  $C=O$  group has the electronic structure  $C\ddagger=O$  as in all ketones, and that consequently *the end of one of the double bonds of Formula I attached to the  $C-OH$  carbon atom is positive*. The very fact of tautomerism rests in the equilibrium between the electrical forces

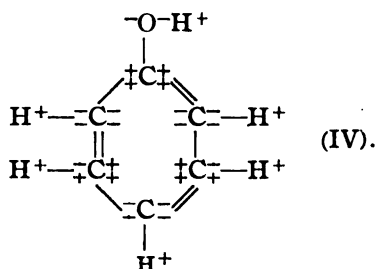


Further, there is a well-known noteworthy tendency of all atoms to become either wholly negative or wholly positive, intermediate forms being relatively unstable and tending to revert to the extremes. This is shown by such well-known reactions as the simultaneous formation of chlorides  $Me^+Cl^-$  and chlorates  $Me^+-O-Cl\ddagger\ddagger\ddagger O_2^-$  and perchlorates  $Me^+-O-$ .

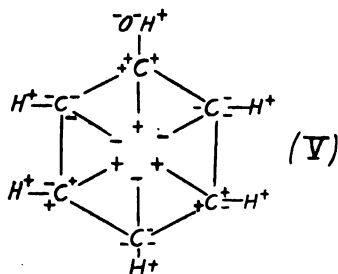
<sup>27</sup> Herzig and Zeisel, *Monatsh.*, 9, 217, 882 (1888); 11, 291 (1890).

<sup>28</sup> See below in regard to the oscillation of the double bond and the centric system.

$\text{Cl}^+ \text{---} \text{O}_2^-$  from hypochlorites  $\text{Me}^+ \text{O}^- \text{Cl}^+$ ; of sulfides and sulfates from sulfites, etc., all through intermolecular oxidation and reduction, *i. e.*, migration of electrons. These relations are of course in perfect harmony with the fundamental conceptions of Thomson, Lewis, Langmuir, and others in regard to the stability of the atoms provided with 8 electrons in their valence "shell." We can conclude, therefore, exactly as in the case of propylene, that both in acetoacetic ester and in phenol *both* of the bonds in the double bond of the enol are positive at the C—OH ends. Since in phenol the double bond oscillates (Kékulé, and confirmed by Fry), we have all four valences of the C—OH carbon atom as positive valences. The symmetry of the benzene nucleus having been amply demonstrated experimentally, we thus have for phenol



It is to be distinctly understood that we have oscillations of the double bonds from side to side and that consequently the centric structure represents an intermediate position of the unsaturated valences.<sup>29</sup> For all we



know, this may represent the structure of by far the largest proportion of the molecules of a benzene derivative—but the *chemically active* molecules have the structure IV.

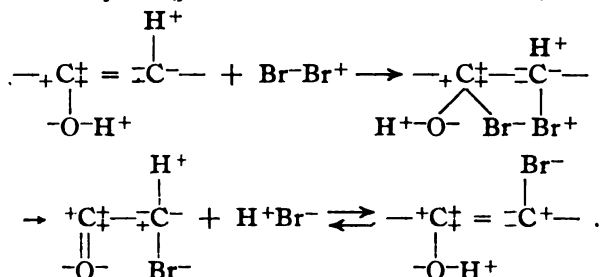
We are now prepared to understand why phenol gives substitution derivatives of the *ortho-ortho-para* series.

Kurt Meyer<sup>30</sup> in an excellent extended investigation has proved that bromination of aceto-acetic ester proceeds quantitatively by absorption of bromine by the enol double bond, followed by the loss of hydrobromic

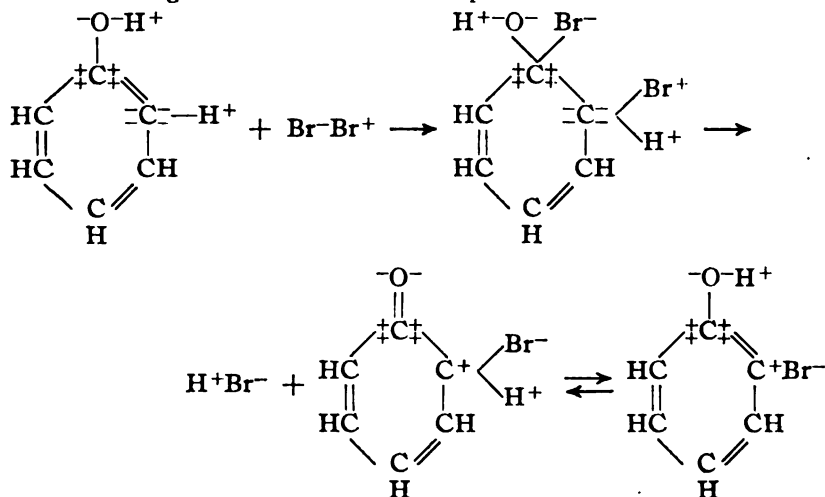
<sup>29</sup> See especially the discussion of H. S. Fry, Ref. 22," on this point.

<sup>30</sup> Meyer, *Ann.*, **380**, 212 (1911); *Ber.*, **44**, 2718 (1911), etc.

acid to form a ketone (not directly a brominated enol). We may now express his results by using the electron valence structures,<sup>31</sup> as

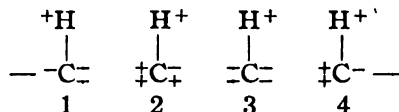


We may apply this proved course of the reaction for aceto-acetic ester without change<sup>32</sup> to the bromination of phenol:<sup>33</sup>



The second *ortho* position is brominated in exactly the same way.

For the *para* reactivity, we have to apply the facts discovered by Baeyer and Thiele which have been summarized in Thiele's theory of "conjugated double bonds" but which need no specific assumptions as to a special kind of double bond to understand their behavior.<sup>34</sup> The fact is simply that a pair of double bonds as in



<sup>31</sup> Subsequently through intramolecular oxidation and reduction the bromine becomes negative and we have as usual  $\text{C}^+ \text{Br}^-$ .

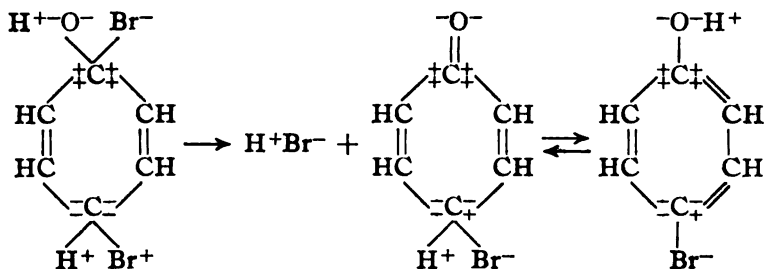
<sup>32</sup> Meyer, *Ann.*, 398, 51 (1913).

<sup>33</sup> Only the essential changes are indicated to save printing.

<sup>34</sup> Cf. Falk and Nelson, Ref. 13, p. 1650.



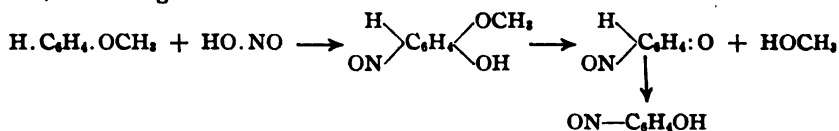
is known to absorb hydrogen, halogen etc., at atoms 1 and 4 and not at 1 and 2, or 3 and 4. Now, in phenol (IV) we have such "conjugated" double bonds and bromine would accordingly be added in positions 1 and 4 to form<sup>33</sup>



Again, by loss of hydrogen bromide a ketone (*para*) is first formed, which reverts to the normal tautomeric enol, *para*-bromophenol (See I and III p.1301).

Similarly, in the nitration of phenol, we have absorption of  $\text{HO}^-$  (or an equivalent anion) and  $^+\text{N}\ddagger\ddagger(\text{O}^-)_2$  at Positions 1 and 2, or 1 and 4, respectively, *ortho*- and *para*-nitrophenol resulting. Nitric acid acts here characteristically through its *basic* ionization,<sup>35</sup> a view which is well confirmed by the use of conc. nitric acid, fuming nitric acid, and conc. sulfuric acid with nitric acid as the best nitrating reagents.

The important feature in the above formulation is to be found in the forces which lead to the location of the *negative ends* of the double bonds in the ring, to which the substituting positive atoms ( $\text{Cl}^+$ ,  $\text{Br}^+$ ,  $^+\text{NO}_2$ , etc.) ultimately go. Whether *simultaneous* additions of *both* components of an absorbed molecule ( $\text{Cl}^-+\text{Cl}$ ,  $\text{HO}^-+\text{NO}_2$ , etc.) to the unsaturated carbon valences must always occur is doubtful and in fact unlikely, and whether the essential feature is not the attraction of the positive substituting group to the negative carbon valences irrespective of complete saturation is a question which will be subjected to further critical work in this laboratory. Kurt Meyer<sup>36</sup> to whom we owe the most profound experimental and theoretical work on this type of substitution has already uncovered at least one important instance where complete saturation, as it is formulated above, must occur. This is in the action of nitrous acid on the methyl ether of phenol, *para*-nitrosophenol being produced and the methoxyl group lost, according to



<sup>35</sup> Cf. Stieglitz, Ref. 12, pp. 288-9.

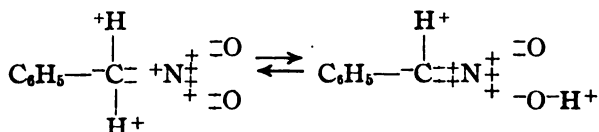
<sup>36</sup> Ref. 32, p. 80.

To what extent similar displacement of the original substituting group in benzene derivatives  $C_6H_5X$  takes place on further substitution, which addition to the positive and negative unsaturated valences obviously makes possible, is not well known and will be studied in this Laboratory.

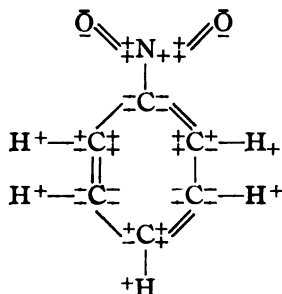
The Crum Brown-Gibson rule of substitution for phenols, favoring *ortho-ortho-para* substitution, rests therefore on the electric structure, IV, of phenol which is here recognized as the favored one because the negative substituting group,  $-O^-$ , develops two positive charges on the carbon atom holding it and these in turn favor complete positive character of the carbon atom in question, in conformity with the universal tendency of a charged atom to be positive or negative, a consequence of the structural relations of the atoms.

The other benzene derivatives  $C_6H_5X$  in which *ortho-ortho-para* substitution is favored, all have a negative X, as  $\bar{N}H_2$ ,  $\bar{Cl}$ ,  $\bar{Br}$ , etc., which has, of course, the same effect as  $\bar{O}H$ .

As to the second group of benzene derivatives  $C_6H_5Y$  in which the formation of *meta-meta* derivatives occurs, we can obtain a similar electron valence basis for the rule by a study of nitrobenzene and its derivatives. From nitric acid  $H^+-O^--N^+ \equiv (O^-)_2$  we obtain the positive nitro group  $+N^+ \equiv (O^-)_2$ . In accordance with this structure we have the well-known nitro-nitronic acid type of tautomerism, established by Hantzsch for phenylnitromethane and for nitrophenol, which we would express electronically for instance in

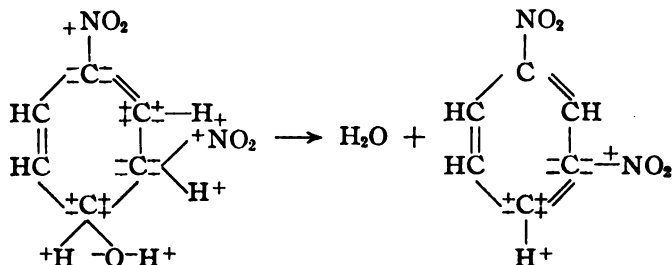


The analogous structure for *para*-nitrophenol is self-evident. It is clear from the nitronic acid formation that a nitro group favors the formation of negative carbon, exactly as oxygen, chlorine, etc., favor positive carbon. We have then as the stable form<sup>37</sup> of nitrobenzene and similar derivatives.



<sup>37</sup> The centric structure as given above is one of the modifications (tautomers) of this electronic structure and perhaps its most stable but *least reactive* one.

We can easily see that in further nitration, *meta*-dinitrobenzene would be the favored isomer<sup>38</sup> formed.



In the same way 1,3,5-trinitro-benzene would be formed. In the other benzene derivatives  $C_6H_5Y$  favoring *meta* substitution, Y is similarly a positive radical as found for  $^+NO_2$ .

In view of the character of the electrical forces involved, it should not be at all surprising that in more complex benzene derivatives we often have competing opposing forces of approximately similar orders of strength, and that mixtures of isomers result—as they always should when we deal with opposing forces of closely related orders of intensity: the well-known equilibrium between an organic acid and an alcohol, an ester and water is an instance of this kind, where the opposing forces are clearly of the same order and we can easily get in quantity derivatives either of the acid or ester, the alcohol or water. It is thought, therefore, that the true basis of the study of the rule of substitution from the point of view of the electronic structure of benzene is best found in the simplest derivatives of benzene. Once the structure is established, the more complex experimental results obtained for more complex derivatives should be used to throw light on the equilibrium relations involved.

### Negative and Positive Halogen Atoms in Organic Compounds

Emphasis should be placed here again on the experimental relations for organic halogen derivatives, which were discussed by the author in a previous article.<sup>39</sup> In the alkyl halides, such as ethyl chloride, ethyl bromide and ethyl iodide we have (non-ionizing) compounds which react uniformly

H  
in accordance with the structure  $RC^+X^-$ ; with water and alkalies, ammonia  
H

and amines, sulfides, alcoholates, we invariably have the negative X replaced by another negative atom as in  $\bar{O}H$ ,  $\bar{N}H_2$ ,  $\bar{N}HR$ ,  $\bar{O}R$ , etc. We never

<sup>38</sup> Only the essential changes are indicated; the others are given in preceding formulas. In place of  $OH^-$  an equivalent anion, e. g.,  $ONO_2^-$ , may be absorbed and split off again, e. g., as  $HNO_2$ .

<sup>39</sup> *Proc. Nat. Acad. Sci.*, Ref. 3.

by any mischance get compounds  $\text{XOH}$ ,  $\text{XNH}_2$ ,  $\text{XNHR}$ ,  $\text{XOR}$ . Jones has shown that in carbon tetra-iodide we have indeed one positive iodine atom,  $(\text{I}^-)_3 \ddot{\text{C}}-\text{I}^+$ , which easily reveals itself by forming  $\text{HOI}$  with water and by the ease with which carbon tetra-iodide is reduced to iodoform. The uniformly negative behavior of the halogen in alkyl halides  $\text{RH}_2\text{C}^+\text{X}^-$  represents, therefore, as definite a guiding force in reactions as do the uniform charges on ionizable atoms in salts, acids and bases; and still alkyl halides are not ionizable, or are so slightly that one could not consider them electrolytes. Yet they show this concrete, specific behavior of polar charges—which proves that ionization and conductivity are not categorical tests for polar valence.

On the other hand, the acyl halogen amides of Hofman, the triaryl-methylhalogen amines of the writer and his collaborators, behave in minute accordance with the electrical structure  $\text{RCO.HN}^-(\text{Hal}^+)$  and  $(\text{Aryl})_3\text{C.HN}^-(\text{Hal}^+)$ ; hydrolysis forms  $\text{HOHal}^+$ , reduction with hydrogen iodide forms free iodine and the amides  $\text{RCONH}_2$  and  $(\text{Aryl})_3\text{CNH}_2$ . Hydroxylamine derivatives  $\text{RCONHOH}$  or  $\text{RCONHOR}$ , and  $(\text{Aryl})_3\text{CNHOH}$  or  $(\text{Aryl})_3\text{CNHOR}$ , are not formed by hydrolysis, by treatment with alkali, alcohol or alcoholates.<sup>40</sup> The molecular rearrangements of these compounds find the most logical explanation in the presence of unstable position halogen atoms as "faults" in the molecule.<sup>41</sup> One cannot escape the fact that the polar structure expresses pointedly and succinctly the whole chemical behavior of these compounds. In exchange for this clean-cut, precise expression of the behavior of whole groups of compounds, one would have to assume *ad hoc* supposititious "tendencies" and give up every advantage of modern knowledge of valence over the old theory of structure and bonds.

### Hydroxylamine Derivatives

The electrical structure of hydroxylamine<sup>42</sup> and its derivatives,  $(\text{H}^+)_2\text{N}^- + \text{O}^-\text{H}^+$  etc., again expresses perfectly the actual behavior of hydroxylamine and its derivatives. It forms salts exactly comparable with salts of ammonia with the analogous structure  $\text{H}^+{}_3\text{N}^-$ ; its positive hydroxyl group is not directly replaceable by  $\overline{\text{Cl}}$ ,  $\overline{\text{Br}}$ , etc., as is the case for the hydroxyl group of bases, of alcohols (which are not *bases* but form oxonium salts<sup>43</sup>) of acids, etc. The positive hydroxyl group in hydroxylamines gives it oxidizing power, and represents a "fault" in the molecule of organic derivatives of hydroxylamine<sup>42</sup> which leads to their well-known rearrangement. Hydroxylamine has also reducing power in common with similar unstable molecules such as hydrogen peroxide, hypochlorous acid, hydrazines, etc. Most important of

<sup>40</sup> Lengfeld and Stieglitz, *Am. Chem. J.*, **15**, 215, 504 (1893).

<sup>41</sup> Stieglitz and collaborators, Ref. 3.

<sup>42</sup> Stieglitz, *THIS JOURNAL*, **36**, 272 (1914), and Jones, *ibid.*, **36**, 1268 (1914).

<sup>43</sup> Their behavior is often misrepresented as that of hydroxide bases.

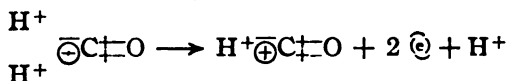
all, the polar structure explains in a most beautiful fashion the occurrence as well as the chemical behavior of the isomeric derivatives discovered by Meisenheim and interpreted brilliantly by Jones.<sup>44</sup> It is true Michael<sup>45</sup> has attacked the interpretation of Jones and the writer's support of this interpretation but in doing so Michael has been obliged to make such extraordinary and impossible *ad hoc* valence assumptions that the writer has been quite content to rest the case and leave to critical chemists and the future the decision between the clean-cut, all inclusive presentation of Jones on the basis of polar valence, and the assumptions of his opponent.

### The Structure of Acids. Oxidation and Reduction<sup>46</sup>

The whole behavior of organic acids and their derivatives is very accordingly understood on the basis of the electronic structure  $\text{RC}\overset{\pm}{\underset{\pm}{\text{C}}}\overset{\pm}{\text{O}}\text{--H}^+$ .

Thus, the enol-tautomerism, *e. g.*,  $\text{RC}=\overset{\text{H}}{\text{C}}\begin{matrix} \text{OH} \\ \text{OH} \end{matrix}$  favoring chlorination in the  $\alpha$  position, the absorption reactions of the  $\text{C}^{\pm}=\text{O}$  group (water, alcohols, sodium alcoholates, ammonia, magnesium alkylhalides, etc.) which differentiate the action of esters as compared with ethers  $\text{R-O-R}$ , are instances of this kind.

The structure also follows from the fact that electrical currents (a flow of electrons) can be obtained by oxidation cells in which alcohols or aldehydes are the sources from which electrons for the current are obtained,<sup>47</sup> producing acids. For instance,<sup>48</sup>



is the essential step in the oxidation of formaldehyde to formic acid. The other steps (union with  $\text{OH}^-$ ) are sequels.

Nevertheless, in recent years we have again and again proposals from the eminent leaders in the field of chemical atomistics, such as J. J. Thomson,<sup>49</sup> the founder of our modern school of thought, G. N. Lewis, Langmuir, etc., to the effect that acids have a non-polar structure to the extent that sulfur

<sup>44</sup> Ref. 42, p. 1284.

<sup>45</sup> Michael, *THIS JOURNAL*, 42, 1232 (1920).

<sup>46</sup> This part of the present report was presented before the Chicago Section of the American Chemical Society in May, 1921. Cf. Chapters xiv and xv, in Vol. I of the author's "Qualitative analysis," Century, Co., 1912.

<sup>47</sup> Stieglitz, *Science*, 27, 774 (1908).

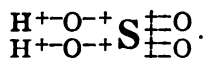
<sup>48</sup> The point where the electrons escape is indicated by  $\ominus$ . Cf. Stieglitz, Ref. 47 in regard to the intermediate formation of  $\text{H}^+\overset{+}{\text{C}}\text{--OH}$  which is the real tautomer  $\ominus$

losing electrons where they are *free* to escape (exactly as in the case of ions such as  $\text{I}^-$ ,  $\text{S}^{2-}$ ,  $\text{Fe}^{++}$ , etc.).

<sup>49</sup> Ref. 2.

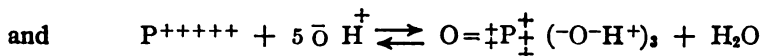
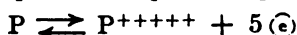
in sulfuric acid, phosphorus in phosphoric acid, etc., are bound to oxygen in a non-polar fashion.<sup>60</sup> Indeed, in this the difference in the ionization of acids and bases is sought.<sup>49</sup>

Now, there are two fundamental sets of experimental facts of record which should be kept in mind in this connection, besides the above exposition of the polarity of organic acids. The first of these is Faraday's observation<sup>61</sup> that electrolysis of very concentrated sulfuric acid deposits *sulfur* at the *negative* pole. Helmholtz very properly considers that conclusive evidence of the positive character of the sulfur in sulfuric acid<sup>61</sup> and we would give it in accordance with his own clearly expressed views the structure



The deposition of sulfur at the negative pole is another beautiful illustration of the power of *basic* ionization<sup>62</sup> of even our strongest oxygen acids. This would be favored in concentrated acid solution. Presumably there is sufficient ionized sulfur sulfate<sup>63</sup>  $\text{S}^{\ddagger\ddagger} (\text{SO}^-)_4$ , formed to make the formation of sulfur in Faraday's experiment a perfectly normal action. The *oxidizing* power of conc. sulfuric (and nitric) acids as against the much lower oxidizing power of the dilute acids is further evidence of polarity because it is essentially the exposed (ionized), positive charges of atoms which absorb electrons (oxidize) in intermolecular oxidation and reduction, as shown by oxidation and reduction potential studies.

The second experimental set of facts to which attention should be called in connection with the problem under discussion is found in the extremely interesting studies of Bird and Diggs<sup>64</sup> on the formation of oxidation-reduction cells with white phosphorus. Not only does phosphorus produce a current (give up its electrons) exactly as any metal that is well known to form a current by the discharge of electrons from its atoms (*e. g.*,  $\text{Zn} \rightarrow \text{Zn}^{++} + 2\text{e}^-$ ) but the potential is subject to the very equilibrium conditions which follow from the polar conception of phosphoric acid. We have



It is evident that added acid, through the suppression of hydroxide ion should favor the presence of  $\text{P}^{+++++}$  in solution and consequently reduce the potential, exactly as the presence of  $\text{Cu}^{++}$  in solution reduces the solution-tension potential of copper. On the other hand, added alkali should sup-

<sup>60</sup> Cf. Lewis, Ref. 6, p. 778.

<sup>61</sup> Cf. Helmholtz, Faraday Lecture, *J. Chem. Soc.*, 39, 277 (1881); see p. 290.

<sup>62</sup> Stieglitz, Ref. 12, pp. 283-289.

<sup>63</sup> Besides  $(\text{SO}_3^{++})\text{SO}_4$ , comparable with uranyl nitrate  $(\text{UO}_2)(\text{NO}_3)_2$ , etc.

<sup>64</sup> Bird and Diggs, *THIS JOURNAL*, 36, 1382 (1914).

press  $P^{\ddagger\ddagger\ddagger+}$  and increase the potential. Both of these consequences of the polar structure of phosphoric acid—and of its ionization as both acid and base—were confirmed experimentally by the work of Bird and Diggs.

The alternative hypothesis of non-polar union would be that phosphorus, in the face of its powerful tendency to discharge electrons, to be oxidized, resumes from, or shares with, oxygen electrons which oxygen itself has a tremendous tendency to absorb and hold, and would form<sup>55</sup>  $O:P(O-H)_3$ . This hypothesis is not only contradictory to the very obvious, powerful tendencies mentioned but fails to account for the equilibrium results of Bird and Diggs. It seems to the author that the polar valence theory has the very decided advantage of summarizing the chemical behavior, without a single new assumption, in a very complete and definite way.

Of particular weight is the following further analogy. It is well known that in the case of inorganic substances, oxidation (escape of electrons) occurs at ordinary temperature particularly readily where we have electrons *free* to escape, as in the case of the valence electrons of atoms ( $Zn$ ,  $H$  *versus*  $H_2$ ) or of ions ( $Fe^{++}$  *versus*  $FeSO_4$ ,  $S^-$  *versus*  $H_2S$ , etc.). Reduction in the same way occurs where we have either exposed positive charges of ions ( $Ag^+$  *versus*  $Ag(CN)^{-}_2$ ,  $Cu^{++}$  *versus*  $Cu_4H_2O_6^{--}$ , etc.) ready to absorb electrons, or where we have exposed electron valence "shells" of free atoms ( $N$  *versus*  $N_2$ ,  $O$  *versus*  $O_2$ ) ready to absorb electrons. Atoms in combination, it is well known, are far less active as oxidizing and reducing agents than in free atomic or ionic forms.<sup>56</sup> In organic compounds we observe exactly the same fundamental characteristic<sup>57</sup>—an exposed free valence is far more reactive in discharging or absorbing electrons (being oxidized or reduced) than a valence bound by union with another atom. In organic compounds we have such exposed valences (comparable with inorganic ions and atoms) in the case of double bonds opening under the stress of the double bond union  $C^{\ddagger}_2 \rightleftharpoons C^{++}C^-$ , also for triple bonds, in the case of bivalent carbon atoms  $RN=C$  and  $H^+-C^+-OH$ , of trivalent carbon

$(C_6H_5)_3C$ , and of the more readily ionizable metal derivatives of carbon,  $ZnR_2$ , etc. Such organic compounds may be used for the preparation of oxidation-reduction electrolytic cells, subject to exactly the same limiting conditions as inorganic compounds. In either case only the exposed charges of a double bond, a methylene carbon atom, etc., or of an ionizable metal atom or a free ion (such as  $Fe$ ,  $Fe^{++}$ , etc.) must be considered to be the sources from which electrons flow, or into which they enter, in oxidation and reduc-

<sup>55</sup> Lewis, Ref. 1, p. 778: Only the essential valences are indicated.

<sup>56</sup> References and a detailed discussion are found in Chapters XIV and XV of the author's "Qualitative Analysis," 1912.

<sup>57</sup> Stieglitz, Ref. 47, p. 774; Ref. 12, p. 289; and *Proc. Inst. Med.*, Chicago, 1, 41 (1916-17).

tion. The free inorganic ions are known to be polar and there is no reason why their organic equivalents, the carbon valences which show exactly the same behavior in oxidation and reduction should not also have a similar electronic, *i. e.*, polar, structure.

There is ample further support of the important role played by polarity in the behavior of organic compounds, such as the difference in behavior of the odd and even numbered chains of carbon atoms in the case of such compounds as the dicarboxylic acids and similar derivatives but it has seemed best to confine this discussion to those groups of compounds in which the writer has been actively interested.<sup>53</sup>

We have thus seen that the polar version of the molecular rearrangement of *bis*-triphenylmethyl-hydrazine is from the point of view of the oxidation and reduction relations involved, far more direct and explicit than the non-polar version, although the latter could be used to arrive at the same net result arithmetically. Similarly, the electrolytic reduction of sulfuric acid to sulfur, the formation of phosphoric acid from phosphorus and of any organic acid from its aldehyde or alcohol in the development of an electric current in which phosphorus, aldehyde or alcohol, respectively, is used as the source of electrons, point unqualifiedly to polar valences rather than to non-polar union.

Similarly, the evidence of directing forces in the absorption by double bonds of organic compounds, in the formation of position isomers, in the occurrence of electromers as shown by L. W. Jones, all demand emphatically the application to organic molecules of polar valences produced by the shifting of electrons from one atom to another.

On the other hand, a difference in the properties of such extreme polar substances as sodium chloride, water, etc., and the corresponding properties of many polar organic compounds must be evident. Exactly wherein the difference lies—possibly expressed in the views of Bohr<sup>6</sup>, Lewis<sup>6</sup> and Kossel<sup>7</sup>—is a subject of chemical and physical investigation in atomistics. Here it is sufficient to point out that it is unfortunate that one and the same word is used to express the two kinds of polarity. The attempt to escape from the resulting confusion of thought by emphasizing the non-polar character of organic compounds when they really show distinctly polar behavior has added confusion to confusion. Polarity exists wherever there is a difference in charge, positive and negative, between two atoms and it is so valuable a conception in the treatment of organic compounds that it must be clearly insisted upon. The author would suggest that in spite of the clumsiness of the term, Thomson's "intramolecular-ionization" as applied to sodium chloride, water and similar extreme polar compounds, does express exactly the presumable difference between the

<sup>53</sup> See also, the persistent differentiation of nitrous acid nitrogen  $N^{+++}$  and ammonio-nitrogen  $N^{=}$  in the diazo compounds, Stieglitz, *THIS JOURNAL*, 30, 1798 (1908).



polarity of the extreme type represented by sodium chloride and the polarity of organic compounds, which is insisted upon in this discussion. Perhaps the use of Thomson's descriptive term for such extreme polar substances will give to organic chemistry the full value of polar conceptions and avoid confusion with the type represented by our common electrolytes.

### Summary

The evidence in favor of the application of the theory of polar *versus* non-polar valences in organic compounds has been considered in various groups of derivatives, with the following results.

1. In the molecular rearrangement of a hydrazine  $(C_6H_5)_2CNH.NH(C_6H_5)_2$ , the theory of polar valence gives an evident cause for the rearrangement, revealing a "fault" in the molecule, and it also makes evident the intramolecular oxidation and reduction of certain atoms, which the experimental results demand. These are fundamental advantages of the theory of polar valences as against that of non-polar valences in carbon derivatives.

2. Exactly the same invaluable advantages are to be found in the theory of polar valences in the study of the analogous molecular rearrangements of chloro- and bromo-amides, of hydroxylamine derivatives, peroxides, etc.

3. In the wholly one-sided absorption reactions of carbon dioxide  $O:C:O$  and of innumerable organic compounds containing unsaturated groups  $C:O$ ,  $C:S$ ,  $C:N$ , polar valences are recognized as the uniformly directing forces.

4. Similar directing forces are observed in absorptions by olefins in which polar valences exist in carbon-to-carbon unions. Exceptions to one-sided absorptions, as in the absorption of bromine chloride, are discussed and accounted for.

5. The Crum Brown-Gibson rule of substitution in the benzene series is developed as the result of a polar electronic structure for benzene, which does not require the assumption of negative hydrogen  $H^-$  (Fry) and is based on the application to benzene of results firmly established in the aliphatic series.

6. The different behavior of negative halogen (*e. g.*, in  $RX^-$ ) and of positive halogen (*e. g.*, in  $RNHX^+$ ) is emphasized as further important evidence favoring polar valences even in the absence of ionization.

7. Advantages of the polar structure for hydroxylamine and its derivatives are summarized.

8. Evidence of the complete polar structure of acids, such as sulfuric, phosphoric acids, and of the carboxyl group of organic acids, is found in:

- (a) Faraday's observation of the deposition of sulfur at the negative electrode in the electrolysis of conc. sulfuric acid.

- (b) The work of Bird and Diggs on the use of white phosphorus as the equivalent of a metal for the production of an electric current.

(c) The production of currents by the use of organic compounds as the source for the escape of electrons in oxidation-reduction cells.

9. It is pointed out that in the oxidation and reduction of organic compounds at ordinary temperature the same general laws hold as for inorganic compounds, namely, that *exposed* valences in organic compounds on double and triple bonds, in bivalent and trivalent carbon, etc., are the common seat of oxidation and reduction reactions, especially at ordinary temperature, exactly as the exposed valences of free ions, free atoms, etc., of inorganic compounds have been found to be.

10. While polarity in organic compounds is insisted upon as giving us an invaluable guide in following organic reactions, it is pointed out that the polarity need not be of the extreme character shown by common salts but may very well be of the character proposed by Bohr, Lewis and Kossel, where the transfer of electrons from atom to atom is not as complete as in the case of common electrolytes. Polarity exists, nevertheless, and the application of the theory of polar valence represents a decided advance in the interpretation of reactions of organic compounds.

CHICAGO, ILLINOIS

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[CONTRIBUTION FROM THE MELLON INSTITUTE OF INDUSTRIAL RESEARCH, UNIVERSITY OF PITTSBURGH]

## THE SOL-GEL EQUILIBRIUM IN PROTEIN SYSTEMS<sup>1</sup>

BY ROBERT HERMAN BOGUE<sup>2</sup>

Received January 21, 1922

### Introduction

The significance of a transitional temperature in gelatin solutions recently has been receiving much attention from chemists. In a general sense it has long been recognized that whereas very dilute solutions (1.0%) of pure gelatin would gel at low temperatures (10°), yet that above certain temperatures, roughly placed at about 35°, gelation would not take place at any concentration. Exceedingly viscous solutions might be obtained, but the ability of these to congeal to a jelly was not observed above this temperature.

In a sense, the melting point of a gelatin or glue has been taken as the critical temperature, as is the case with crystalloids, but melting point is not at all easily obtained or even defined when such substances as gelatin are under consideration. Many attempts have been made to determine this property, but none of them may be regarded as absolute melting-

<sup>1</sup> Presented before the St. Louis Section of the American Chemical Society, March 6, 1922.

<sup>2</sup> Industrial Fellow, Mellon Institute of Industrial Research, Pittsburgh, and Research Chemist for Armour and Company, of Chicago.

point determinations in the classical conception of the term. A very appreciable time factor enters into the above determinations which prevents an exact coincidence of the melting and solidification or setting points. The fact must be met that in such systems as these the transition from the hydro-sol to the hydro-gel condition is continuous, as far as our ability to measure the "point" of change is concerned, and to quote Sheppard,<sup>3</sup> "both the 'melting point' and the 'setting point' are more or less arbitrary conceptions, and their determination depends mainly upon standardized experimental conventions."

In a study upon the mutarotation of gelatin C. R. Smith<sup>4</sup> has shown that at temperatures above 33° to 35° the specific rotation of gelatin is practically constant at about -123°, while at temperatures below 15° the specific rotation is practically constant at about -266°. At all temperatures intermediate between 35° and 15° the rotation varies between these two limits. Smith arrives at the conclusion that gelatin in aqueous solution exists in two modifications; the one stable at temperatures above 33-35° which he denotes as Sol form A, and the other stable at temperatures below 15° which he denotes as Gel form B. "Between these temperatures a condition of equilibrium between the two forms exists and the mutarotation observed seems to be due to the transformation of one form into the other by a reaction which is reversible with temperature."

Bingham and Green<sup>5</sup> have made exhaustive studies of the laws and measurement of plastic flow, and the applications of plastic flow to industrial processes, and Bingham<sup>6</sup> has described a variable pressure method for the measurement of viscosity.

It has been shown that a *viscous liquid* will start to flow no matter how small a pressure is applied. With *plastic materials* no flow takes place until after the pressure has exceeded a certain definite value. Bingham points out that when viscosity determinations are made by noting the volume of outflow of the liquid in a given unit of time, and this volume is plotted against a variable but rigidly controlled and accurately measured pressure, an extension of the curve to the axes will pass through the origin, or zero point of the axes, provided the substance obeys the laws of a truly viscous liquid, but that the extension of the curve will fall upon the pressure axis at a finite distance ( $f$ ) from the volume axis if the substance is a plastic solid. This distance ( $f$ ) he calls the *yield value* and defines as the force required to start the flow.

It seems that equally comparable, although perhaps less sensitive measurements for the determination of the viscosity-plasticity relations may be made by the use of a torsional viscosimeter of the MacMichael type. By varying the speed of rotation of the cup the same effect is produced as by varying the pressure in the capillary tube type of instrument. A study of gelatin solutions was conducted by this method.

<sup>3</sup> Sheppard and Sweet, *J. Ind. Eng. Chem.*, 13, 423 (1921).

<sup>4</sup> Smith, *THIS JOURNAL*, 41, 146 (1919); *J. Ind. Eng. Chem.*, 12, 878 (1920).

<sup>5</sup> Bingham, *Bur. Standards Bull.*, 13, 309 (1916-17). Bingham and Green, *Proc. Am. Soc. Testing Materials*, 19, 640 (1919). Green, *ibid.*, 20, 451 (1920).

<sup>6</sup> Bingham, *ibid.*, 18, Pt. 11, 373 (1918).

### Viscosity-plasticity Studies

The procedure adopted was as follows. Several lots of the highest quality of granulated gelatin were employed in the tests. These were made up accurately into 10, 20 and 25% solutions by soaking in cold water for 1 hour, dissolving in a water-bath at 70°, again making up accurately all water lost by evaporation and, with no delay, introducing into the cup of the viscosimeter. The latter was at the same temperature as the

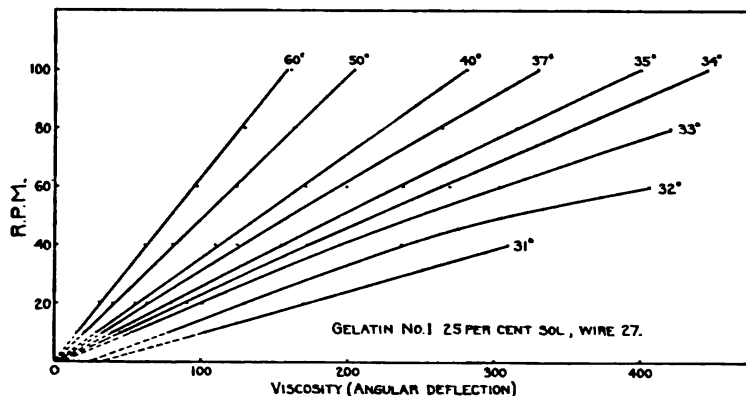


Fig. 1.—Viscosity-plasticity curves.

gelatin solution, and was immersed in the water-bath, which is a part of the instrument, at a temperature of 70°. The heating process for bringing the gelatin into solution was made as brief as possible. The cover of the instrument was kept on the cup to prevent evaporation during the measurements.

The solution was kept thoroughly stirred by lifting the plunger up and down, and the temperature permitted (by use of the electric heating unit)

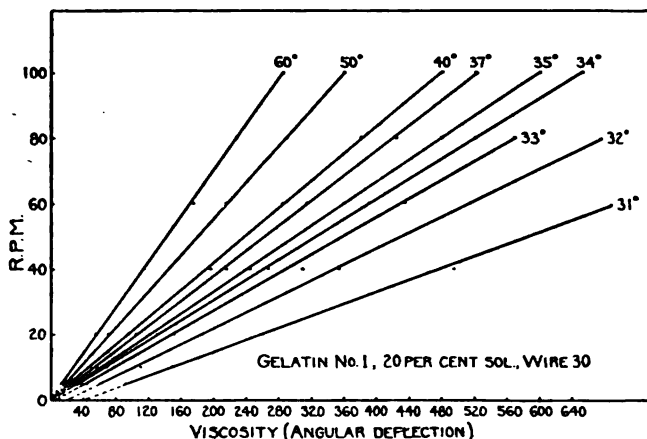


Fig. 2.—Viscosity-plasticity curves.

to fall very slowly. The viscosity was taken intermittently at definitely indicated temperatures as the solution cooled until it became too viscous to measure.

The velocity of rotation of the cup was very carefully adjusted before and after the measurements. Each series, as above, was measured at

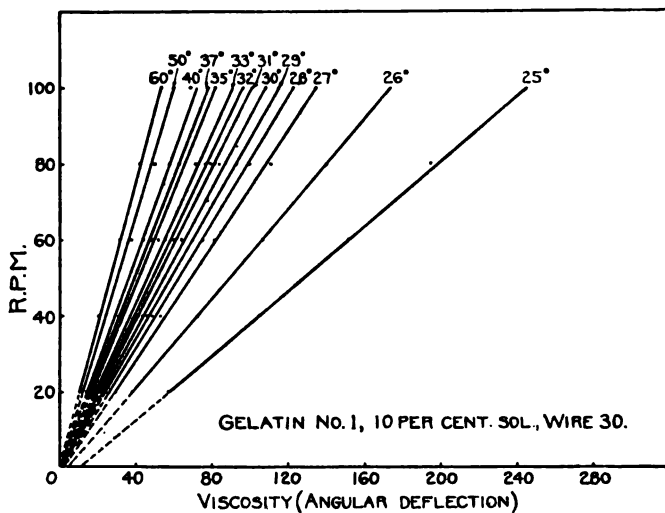


Fig. 3.—Viscosity-plasticity curves.

the same velocity of rotation throughout the temperature range from 60° to 31° or lower, and then the velocity changed. Speeds from 5 to 100 r.p.m. were used.

The whole process was repeated for the three concentrations used, and again repeated with the employment of differently sized wires in the instrument.

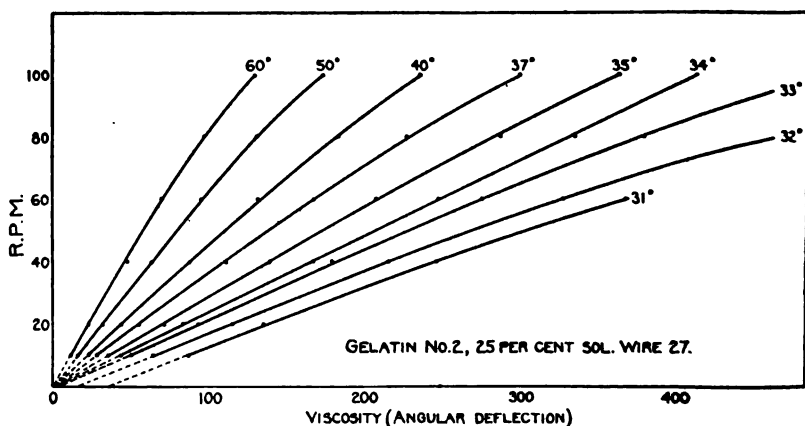


Fig. 4.—Viscosity-plasticity curves.

Some of the data obtained are shown in graph form in Figs. 1 to 4.

In the curves the velocity of rotation is plotted against angular deflection. An examination of these graphs shows that by continuing each curve downward until it intercepts the axis two conditions are made manifest. In one of these conditions the origin of each curve is the zero point of the axes. In general, all curves plotted from temperatures higher than  $34^{\circ}$  are of this type. In the other condition, the origin of the curves lies at some point on the viscosity axis at a varying distance from the ordinate representing r.p.m. The lower the temperature, the further is the point of interception with the abscissa removed from the convergence point of the axes.

This seems to mean, arguing from the geometry of the graphs, that in those cases where the intercept lies on the abscissa an infinitely small velocity of rotation will result in a viscosity deflection of finite magnitude. That is, the gelatin, under those conditions, offers a permanent and fixed resistance to deformation. It is an elastic body; it possesses a measurable degree of rigidity; and deformation may not occur until after a certain minimum of pressure, exerted against it, has been exceeded. These are, as a matter of fact, the very attributes which are characteristic of plastic substances.

If it were necessary to carry the analogy further we might say that the distance from the origin of the axes to the point of intersection corresponds very closely to, although it is not identical with, the yield value,  $f$ , as obtained by Bingham's method. The magnitude of this distance may correctly be taken as a measure of the plasticity of the material.

It will be observed that at velocities of rotation above 60 r.p.m. there is in some cases a slight bending of the curves, away from the velocity axis. That is, at the higher speeds of rotation, the observed viscosity is somewhat greater than should obtain if the lower (straight) portion of the curve may be regarded as most correctly expressive of the true theoretical values. The reason for this bending is undoubtedly to be found in an instrumental error by which eddy currents are set up within the liquid when the velocity exceeds a certain value. There is also very probably produced at the higher velocities a slipping of the liquid along the sides of the cup causing it to move to a greater degree *en masse* rather than with the telescopic shear of a truly viscous flow.

Above a certain temperature (at any given concentration) the curves follow the laws of truly viscous flow, *e. g.*, they converge, when extrapolated to the axes, at the origin. In other words the observed angular deflection is directly proportional to the speed of rotation. At a given temperature (for a given concentration), however, and at all temperatures below this point, the curves follow the laws of plastic flow as above pointed out. Our "solution" of gelatin behaves, therefore, as a viscous liquid

at elevated temperatures, and as a plastic solid at low temperatures (but still above the solidification point).

If we may accept C. R. Smith's conclusions that above 33–35° the sol form only may exist, while below that temperature increasing amounts of the gel form are in equilibrium with the former until at 15° the gel form only is stable, then it seems to follow from the data here presented that gelatin sol is a viscous liquid while very small amounts of gelatin gel are sufficient to impart to the "solution" the property of plastic flow.

### The Sol-gel Equilibrium

The writer<sup>7</sup> has already pointed out that gelatin sols appear to consist of molecules which, upon a lowering of the temperature, tend to cohere into aggregates in the form of catenary threads of more heavily hydrated molecules. Further evidence in support of this viewpoint is given in the following paper on "The Structure of Elastic Gels."<sup>8</sup> We will add at this place, however, that the resiliency or elasticity of the jelly seems to be dependent upon the length of these threads. And apparently elasticity in the gel state is synonymous with plasticity in the fluid condition, for, on account of the amicroscopic or ultramicroscopic size of these particles and the short threads characteristic of the sol state, any displacement of them in the fluid would meet with so great a frictional resistance that the property of elasticity, or plastic flow, would be transmitted to the whole mass. This is what is observed when the curve of viscous flow changes to one of plastic flow.

None of the instruments that have been devised for measuring molecular or molecular group elasticity (plasticity) is in any sense absolute; *e. g.*, there is a sensitivity coefficient below which they cease to function. In other words, while we can say definitely that paint for example, is a plastic solid or shows properties of plastic flow, we cannot say as positively that water exhibits no such properties. All that we may say is that, as far as the most delicate sensitivity of our instrument reveals, there is no indication of plastic flow in water. Theoretically there is no reason to believe that liquid water (dihydrol) should not possess intermolecular elasticity.

With the instrument used in the foregoing experiments (the Mac-Michael viscosimeter) the highest temperature at which evidences of plastic flow were observed (in 25% concentration) was about 34°. A more delicate instrument might show this property at a higher temperature. As the concentration of the gelatin solution was decreased, the maximum temperature at which plastic flow was first observed became lower, *e. g.*, about 33° in the 20% concentration, and 29° in the 10% concentration.

<sup>7</sup> Bogue, *Chem. Met. Eng.*, 23, 62 (1920).

<sup>8</sup> Bogue, *THIS JOURNAL*, 44, 1343 (1922).

This is in entire conformity with the argument presented above; for while it was stated that the plasticity was probably an expression of inter-fibrillar elasticity, and that elasticity seemed to be determined by the length of the fibrils, it also follows, from the limited sensitivity of our apparatus, that the measurability of this property must depend upon the actual concentration of fibrils in the solution, and this is proportional to the total concentration of gelatin in the solution at any given temperature.

Davis<sup>9</sup> has reported that at the temperature of 38.03° gelatin sol and gel can exist in equilibrium, while this is not true for any other temperature. That is, a "seeded" solution (one to which a little gelatin gel had been added) showed no change in viscosity with time at the temperature of 38.03°. At any temperature below this a regular increase in viscosity with time was observed. At higher temperatures a decrease occurred until the viscosity equaled that of a similar unseeded portion at the same temperature. Sheppard<sup>10</sup> has been able to corroborate this value very closely.

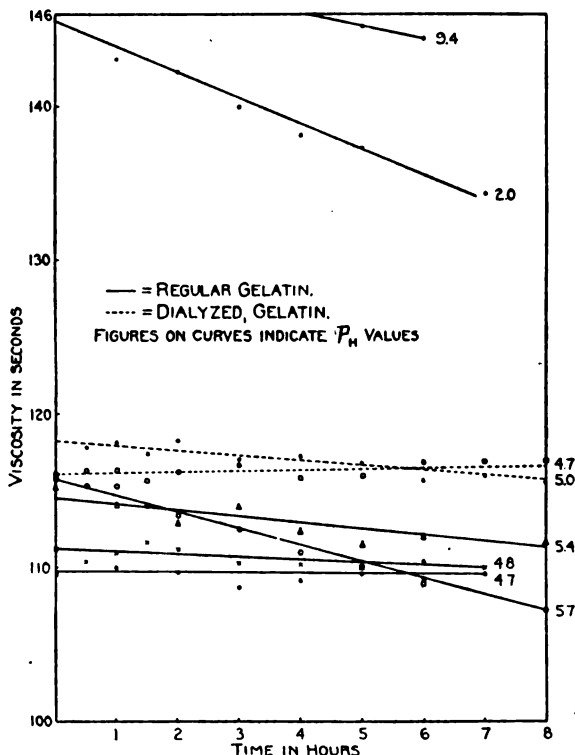


Fig. 5.—Change in viscosity with time at varying  $P_H$ ; 2% solution, 35°.

<sup>9</sup> Davis and Oakes, *THIS JOURNAL*, **44**, 464 (1922).

<sup>10</sup> S. E. Sheppard, discussion at 62nd Meeting, American Chemical Society, New York, Sept. 6-10, 1921.



but Loeb<sup>11</sup> has reported that at any temperature above 35°, the viscosity (of a 2% solution of gelatin chloride of Sørensen value,  $P_H$  2.7) *decreases* on standing.

In order to bring more data to bear upon this point a series of experiments was performed with the object of noting the changes in viscosity with time of gelatin solutions of varying hydrogen-ion concentration and of varying gelatin concentration. The varying degrees of hydrogen-ion concentration were obtained by soaking the granulated gelatin in cold hydrochloric acid or sodium hydroxide solutions of the proper strength, for 1 hour, then washing out the excess electrolyte as directed by Loeb, and making up to 2% concentration. Portions of this were also diluted to 1 and 0.5% concentrations and viscosity tests made with an Ostwald viscosimeter at frequent intervals for 8 hours. The temperature was rigidly controlled at 35.0°. The data, shown in part in Fig. 5, indicate a decrease in viscosity with time at every hydrogen-ion value tested, from  $P_H$  2.0 to  $P_H$  9.4, with the exception of the sample at  $P_H$  4.7 in which case there was no change. The sample at  $P_H$  4.8 was "seeded," but no alteration in the slope of the curve was observed. The nearer the hydrogen-ion concentration of the samples to the iso-electric point, the less was the variation in viscosity with time. There was in no case, however, an increase in viscosity with time.

A gelatin that had been purified by dialysis was next subjected to the same treatment, and although the curves were in most instances very similar to the previous ones, yet at  $P_H$  4.7 there was a slight tendency for an increase in viscosity with time as indicated by the dotted curves in Fig. 5. At 37.0° the curve was again horizontal.

The significance of these data is now apparent. There are obviously many factors which influence the effective volume of the gelatin in the solution. Of these the hydrogen-ion concentration seems to be most important. The amount and nature of the inorganic ions with which the gelatin is associated is another. The presence of the hydrolysis products of gelatin is a third factor, and the measurability of these influences will be determined by the concentration. At low temperatures, *e. g.*, 25°, the tendency in the system is for an increase in the size of the molecule aggregates; hence an increase in viscosity with time. At high temperatures, *e. g.*, 40°, the tendency is for a decrease in the size of these aggregates. Hence a decrease in the viscosity with time. At any specific temperature, *e. g.*, 35°, whether the aggregates will become larger or smaller is determined by the hydrogen-ion concentration of the solution, and the presence of inorganic ions and protein hydrolysis products. Under any given set of conditions there will be some temperatures at which neither increase nor decrease will occur. This point was found in gelatins studied

<sup>11</sup> J. Loeb, *J. Gen. Physiol.*, **4**, 107 (1921).

by Davis and by Sheppard to be at about  $38^\circ$ ; in gelatins studied by Loeb to be at  $35^\circ$  (in solution of  $P_H$  2.7); and in gelatins studied by the writer to be at  $35^\circ$  and  $37^\circ$  (in solution of  $P_H$  4.7).

It appears that the colloid fibril consists at elevated temperatures of but a few partially hydrated molecules attached to each other, and floating about as discrete particles in the solvent. An increase in viscosity with time would then signify either an increase in the size (length) or number of the threads, or an increased volume due to the absorption of water or hydration. At elevated temperatures, the equilibrium is evidently rapidly attained. This seems to be due to the relatively small changes that are induced in the particle size and degree of water absorption or hydration by variations in temperature at *elevated temperatures*, and to the high mobility of the free solvent. But as the temperature falls, the amount of change per unit drop in temperature rapidly increases, and with this is a rapid decrease in the mobility of the solution through the withdrawal of the solvent by absorption or hydration. The time required for the colloidal molecule-fibrils to reach a state of complete equilibrium with the solvent is consequently vastly increased. In other words the solution will show an increase in viscosity with time.

Under any given condition of temperature and hydrogen-ion concentration there will be a certain condition of viscosity which the system will attain at equilibrium. A temperature at which no change in viscosity with time occurs indicates an immediate equilibrium condition, but this temperature will vary with different hydrogen-ion concentrations and with different degrees of purity of the sample. It is in no way indicative of a critical equilibrium temperature between the sol and gel forms, but is rather only a point on a continuous curve. This may be expressed by the equation

$$\eta_{P_H} = K/f(T)$$

where  $\eta_{P_H}$  is the viscosity at equilibrium at any given hydrogen-ion concentration,  $f(T)$  is some function of the temperature, and  $K$  is a constant. On account of the length of time required to attain equilibrium, and the difficulty of eliminating completely all other influences such as hydrolysis due to the prolonged action of water, electrolytes, or bacteria, the exact measurement of  $\eta_{P_H}$  is uncertain, except where the conditions have been met for the existence of an equilibrium *immediately*. This is the condition encountered where that temperature is obtained at which no change in viscosity with time is observed.

The idea of a gradual rather than an abrupt change on passing from the sol to the gel form is further indicated by the finding of Walpole<sup>12</sup> that the refractive index of a gelatin-water system is a linear function of the

<sup>12</sup> Walpole, *Kolloid-Z.*, 13, 241 (1913).

concentration, and if plotted against the temperature shows no discontinuity at any point between the liquid sol and the rigid gel. McBain<sup>12</sup> has reported that the sol and gel of soaps differ only through the mechanical rigidity and elasticity of the gel form.

### Summary

Experiments have been conducted upon the viscosity-plasticity relations in gelatin solutions which have indicated (1) that gelatin in aqueous solution as measured by the MacMichael viscosimeter follows the laws of viscous flow at elevated temperatures, and that the same exhibits the properties of plastic flow at lower temperatures (above the solidification point); and (2) that the transition between the sol and gel form does not take place at any given *point* of temperature, but rather extends throughout a rather indefinite *period* of temperature.

The variation in viscosity with time was studied and it was found that at a given temperature (35°) the increase or decrease in viscosity with time was dependent upon the hydrogen-ion concentration, the nature of the inorganic ions present, and the amount of hydrolyzed protein in the system. It is urged that the temperature at which no change in viscosity with time is observable may not be taken as a critical temperature between the sol and gel forms, but rather that, given sufficient time under aseptic conditions, there may be conditions reached at *any* temperature at which there will be no change in viscosity with further lapse of time. The expression, "no change in viscosity with time," means only that the relative volume of the particles of gelatin or gelatin aggregates in the system tends neither to increase nor decrease under the conditions attained. A lowering of the temperature will cause an increase in this relative volume and hence an increase in viscosity, but this increase being attained (after the lapse of time), the viscosity will then again become constant. A rise in temperature will produce the opposite effect. The equation is, therefore, written

$$\eta_{P_H} = K/f(T)$$

indicating that the viscosity of pure gelatin at any given hydrogen-ion concentration is inversely proportional to some function of the temperature, and that, at equilibrium, there will be some viscosity (at any given hydrogen-ion concentration) which will correspond with every point of temperature.

The conclusions indicate that there is no sharp transition point between the sol and gel forms in protein systems, but that the transition is continuous and reversible over a somewhat indefinite period.

The writer wishes to express his indebtedness to Mr. M. L. Sheely of the Armour Glue Works Laboratory for assistance in making many of the measurements reported herein.

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<sup>12</sup> Laing and McBain, *J. Chem. Soc.*, 117, 1506 (1920).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, YALE UNIVERSITY]

## STUDIES ON CATALYSIS. II.<sup>1</sup> DEHYDRATION AND ADDITION REACTIONS OF ETHYL ALCOHOL: THE FORMATION OF ACETAL AND MERCAPTANS<sup>2</sup>

By FRANCOIS A. GILFILLAN<sup>3</sup>

Received January 27, 1922

The results described in the following paper were obtained in an investigation made to determine the comparative activity of the oxides of silicon, thorium, titanium and tungsten in inducing certain catalytic dehydration and esterification reactions with ethyl alcohol in the vapor phase and at comparatively high temperatures.

Ethyl alcohol subjected to dehydration in the vapor phase, may give rise to either or both of two products. With certain catalysts, and at lower temperatures, ether is produced, while under all other conditions a more complete dehydration occurs, with the production of ethylene.

This dehydration was first observed by Priestley<sup>4</sup> while passing alcohol vapors through an earthen tube heated to redness. But it remained for Deimann<sup>5</sup> to observe the catalytic action of the tube itself in this dehydration, and to separate and identify the gases formed. He found that alcohol vapors passing over heated alumina or silica were converted into ethylene, while those passing over heated glass, lime or talc produced none of this gas. The presence of a certain amount of hydrogen in the ethylene was also reported.

Berthelot<sup>6</sup> found that ethyl alcohol could be passed over pumice below 500° without undergoing any decomposition, and Nef<sup>7</sup> found a similar behavior up to 625°. Sabatier and Mailhe<sup>8</sup> reported the use of thoria as a catalyst in 1908 and found that this oxide at 340° gave 50% more ethylene than did alumina. In addition to its greater activity it reacted exclusively as a dehydrating agent<sup>9</sup> and was not rendered inactive by overheating. The recent work of Kramer and Reid<sup>10</sup> shows that under certain conditions, thoria may also exercise an appreciable dehydrogenation on alcohols. And these same investigators have shown, furthermore, that the activity of thoria may be impaired by overheating, which fact has likewise been confirmed by the writer.

<sup>1</sup> Paper I by Johnson and Brown, *Proc. Nat. Acad. Sci.*, 7, 75 (1921).

<sup>2</sup> This paper is constructed from a dissertation presented by Francois Arch Gilfillan in June, 1921, to the Faculty of the Graduate School of Yale University in candidacy for the degree of Doctor of Philosophy. (Treat B. Johnson.)

<sup>3</sup> This work was done under a special grant which was generously contributed by the Calco Chemical Company of Bound Brook, N. J. The writer desires to acknowledge at this time his appreciation of this assistance and to express his thanks to this company for its interest in his work.

<sup>4</sup> Priestley, *Phil. Trans. Roy. Soc.*, 73, 429 (1783), "Experiments and Observations on Air," Vol. 1, p. 200 (Birmingham, 1790).

<sup>5</sup> Deimann, van Troostwyk, Bondt, and Louwrenburgh, *Crell. Ann.*, 1795, II, pp. 312 and 430.

<sup>6</sup> Berthelot, "Traité de chimie organique," 1872, p. 164.

<sup>7</sup> Nef, *Ann.*, 318, 200 (1901).

<sup>8</sup> Sabatier and Mailhe, *Compt. rend.*, 147, 108 (1908).

<sup>9</sup> Sabatier and Mailhe, *Ann. chim. phys.*, [8] 20, 341 (1910).

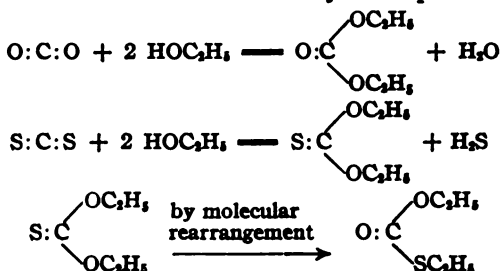
<sup>10</sup> Kramer and Reid, *THIS JOURNAL*, 43, 880 (1921).

Crystalline titanium dioxide, according to Sabatier and Mailhe,<sup>11</sup> shows no catalytic influence on the vapor of primary alcohols at temperatures up to 400°, but the amorphous form of this oxide is an active catalyst<sup>8</sup> and at 320° ethylene is formed. Engelder passed<sup>12</sup> absolute alcohol over amorphous titanium oxide at 490° and obtained a gas which contained 23% more ethylene than that obtained by Sabatier at a temperature 90° lower. He also observed the formation of ethane, the proportion of which in some cases was as high as 55% of the total gas. Titanium oxide, therefore, acts simultaneously as a dehydrating, dehydrogenating, and hydrogenating catalytic agent.

The yellow oxide of tungsten, WO<sub>3</sub>, is reduced at 350° by the vapors of alcohol. This blue oxide, as observed by Sabatier and Mailhe<sup>13</sup>, is an energetic dehydrating catalyst toward alcohols.<sup>9</sup>

It is well known that esterification can be promoted by certain catalysts, especially by sulfuric acid, but it was not until 1911 that catalytic esterification in the vapor phase was accomplished. For this purpose titanium dioxide has proved a much better catalyst than thoria.<sup>14</sup> Even the weak acid hydrogen sulfide may be made to react with alcohols under the influence of catalysts of dehydration. This was first applied by Sabatier and Mailhe<sup>15</sup> in 1910 with thoria, and the same agent has recently been employed for the same reaction by Kramer and Reid.<sup>10</sup>

The main purpose of the present research was to extend this work on esterification by catalysis, and to determine whether or not carbonic esters might be produced by the interaction of ethyl alcohol in the vapor phase with carbon dioxide and carbon disulfide. The chemical changes that were of immediate interest to us may be expressed as follows.



The catalysts employed in our work were pumice, thorium oxide, titanium oxide, and the blue oxide of tungsten, and the results of the investigation are described in detail in the experimental part of this paper. The researches on the study of catalysis will be continued.

### Experimental Part

**The Heating Unit.**—The electric furnace in which all of our experiments were conducted was constructed from an alundum tube 61 cm. long and 4cm. internal diameter. This was wound with a spiral of Ni-chrome ribbon 13.7 meters in length, the ribbon being 3 mm. wide and

<sup>11</sup> Sabatier and Mailhe, *Compt. rend.*, 146, 1377 (1908).

<sup>12</sup> Engelder, *J. Phys. Chem.*, 21, 689 (1917).

<sup>13</sup> Ref. 8, p. 17.

<sup>14</sup> Sabatier and Mailhe, *Compt. rend.*, 152, 496 (1911).

<sup>15</sup> Sabatier and Mailhe, *ibid.*, 150, 1217 (1910).

0.25 mm. thick The reaction tube was of fused silica, 90 cm. long and 16 mm. internal diameter. This tube extended through the alundum tube, and asbestos and magnesia were stuffed at each end into the space between the tubes, so that the silica tube, surrounded by a dead air space, extended through the alundum tube without touching it at any point.

**Reagents.**—The pumice used was a clean, granular product, in pieces of about the size of peas. This was used alone, and also as a support for the other catalytic agents employed.

Four contact masses were prepared from thorium nitrate, in order to observe the effect of method of preparation on the activity of this oxide. In the first instance, pumice was impregnated with a solution of 200 g. of thorium nitrate in 200 cc. of water. One-half of the pumice was dried at 100° and then ignited in a crucible at red heat for 3 hours. This charge, containing 36 g. of thoria, will be designated as Thoria A. The second portion of the impregnated pumice, without previous drying, was suspended in concentrated aqueous ammonia for several hours, then dried at 100°. This charge, prepared by precipitation of the hydroxide on the surface of the pumice, will be designated as Thoria B.

Two contact masses of thoria were prepared by direct precipitation of the hydroxide by treating a solution of the nitrate with ammonia, washing the precipitate until free from ammonia, and then drying it at 130°. One-half of this precipitate was mixed with enough impregnated pumice from Thoria B to bring the total thorium oxide content up to 60 g. This charge will be designated as Thoria C. The last contact mass, prepared and mixed with the impregnated pumice in the same manner, and containing 120 g. of thorium oxide, will be designated as Thoria D. The titanium oxide in portions of 60 g. was mixed with clean pumice before using as a catalyst. The tungsten oxide catalyst was prepared by mixing the yellow oxide of 99.23% purity with clean pumice and reducing with alcohol vapors at 350° to the blue oxide,  $W_2O_5$ . The re-oxidation of this material to the yellow oxide was avoided by excluding air.

The alcohol used throughout the work varied in strength from 98.26% to 99.83%. The carbon disulfide employed was purified by treatment with anhydrous copper sulfate, agitating with mercury, and finally redistilling. The product then boiled constantly at about 46.3°.

### The Dehydration of Ethyl Alcohol

Pumice was found to have no catalytic effect on alcohol at 400°. When passed through the tube at the rate of 30 g. per hour, the recovery represented from 99% to 100% of the weight of the original alcohol used, and an analysis showed the presence of only a trace of acetaldehyde. The presence of carbon dioxide exerted no influence on the reaction, even when the temperature was raised to 500°.

As stated above, several catalytic masses of thoria were employed, the first of these, Thoria A, being prepared by ignition of pumice impregnated with thorium nitrate. Three experiments with this material at temperatures between 250° and 350°, and at rates of flow varying between 22 g. and 70 g. per hour, showed recovery between 98% and 100% of alcohol containing a trace of aldehyde, which, however did not appear when air was displaced from the apparatus by carbon dioxide. Quite different results were obtained by use of the other thoria masses, prepared

without calcining. Thoria C showed at 250° a 92% recovery of alcohol, 90% at 300°, and 77% at 400°. In each instance some aldehyde was shown to be present. Thoria D was used in 5 experiments. At 300°, a recovery of 97% was observed when the rate of passage was 40 g. per hour, but when the rate was lowered to 20 g. per hour, only 93% was recovered. At 350° the same recovery was observed, but at 360°, only 68% was recovered. The catalytic mass was then heated to low redness in the furnace for 18 hours, after which three experiments were performed, in the presence of carbon dioxide. At 325° only a trace of ethylene was obtained, and 98% of the alcohol was recovered. At about 425°, from alcohol passing over the catalyst at the rate of only 15 g. per hour, 82% was recovered.

Results of the above investigation are shown graphically in Fig. 1, in which the curve Thoria A represents catalyst prepared by calcination.

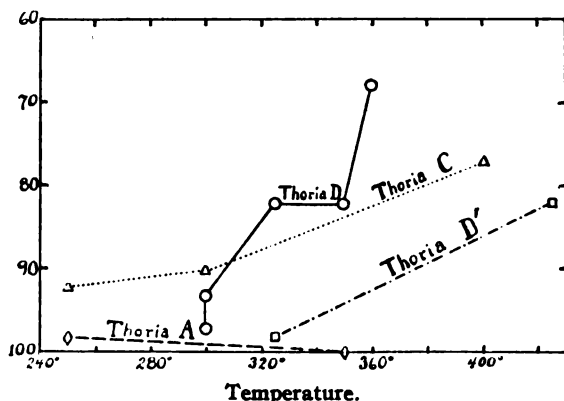


Fig. 1.—Inactivation of thoria by calcination.

The curves Thoria C and Thoria D represent the action of the two samples of catalyst prepared by precipitation, while curve Thoria D' depicts the activity of the corresponding catalyst after having been heated to low redness for 18 hours. It is evident that, contrary to the statement of Sabatier,<sup>16</sup> the catalytic action of thoria is greatly diminished by calcination, or even by prolonged heating at a lower temperature. As would be expected, the amount of catalyst present does influence the rate of activity, as likewise does the rate of passage of the alcohol.

Titanium oxide gave results quite different from those given by thorium oxide. Alcohol passed through the furnace at the rate of 25 g. per hour gave at 325°, 350°, and 355°, a recovery of 98% by weight of alcohol containing small amounts of unidentified substances. When carbon dioxide was passed through with the alcohol at 262° and at 300°, all of

<sup>16</sup> Sabatier, "Die Katalyse," Akad. Verlagsgesellschaft M. B. H. in Leipzig, 1914, p. 170.

the alcohol was recovered unchanged. At 350° and 355°, there was a slight evolution of ethylene, and 98% of the alcohol was recovered. In each of the 7 experiments which were conducted over this catalyst, the recovered alcohol contained a trace of impurity, which decolorized bromine water and gave a slight turbidity when the alcohol was diluted with water. This was soluble in ether but on evaporating the solvent there remained behind an insufficient quantity of material for identification. The above results indicate that the titanium dioxide used in our work had practically no dehydrating effect upon ethyl alcohol, and also that it does not accelerate a reaction between the alcohol and carbon dioxide

The blue oxide of tungsten was found to be the most active of the 4 catalysts investigated, and in the following table are recorded the results of 7 experiments with this oxide. In each experiment 100 g. of alcohol was used and the vaporization was at the rate of about 20 g. per hour.

Temperature ° C.	Recovered alcohol G.	Purity %	Absolute Alcohol recovered G.
275	94	96	90
300	86	87	75
325	82	85	70
360	72	77	55
250	97	98	95
300	82	88	72
350	62	67	42

The last 3 experiments were conducted with a stream of carbon dioxide passing through the tube with the alcohol during the dehydration.

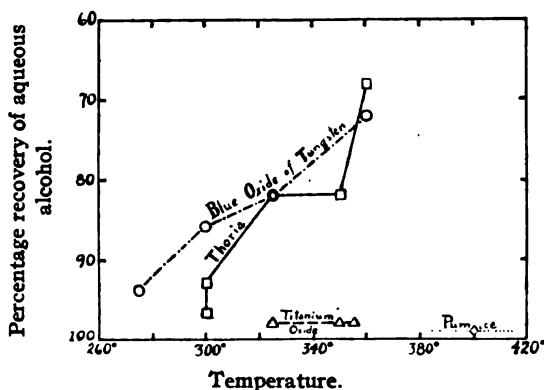


Fig. 2.—Dehydration of ethyl alcohol by various catalysts:

In Fig. 2 are shown curves indicating the amounts of aqueous alcohol recovered when 100 g. of absolute alcohol was led over the various catalysts at different temperatures. Pumice showed no activity at 400°. Titanium dioxide was without action up to 355°, the highest temperature



employed, while thoria and the blue oxide of tungsten decomposed alcohol at temperatures of  $300^{\circ}$  or lower. A comparison of these two catalysts is shown in Fig. 3, where the curves are plotted from data covering experiments in which the recovered aqueous alcohol was analyzed to determine its content of absolute alcohol. From Figs. 2 and 3, it is apparent that at lower temperatures the catalytic activity of the blue oxide of tungsten is greater than that of thoria, although at higher temperatures they approach the same value.

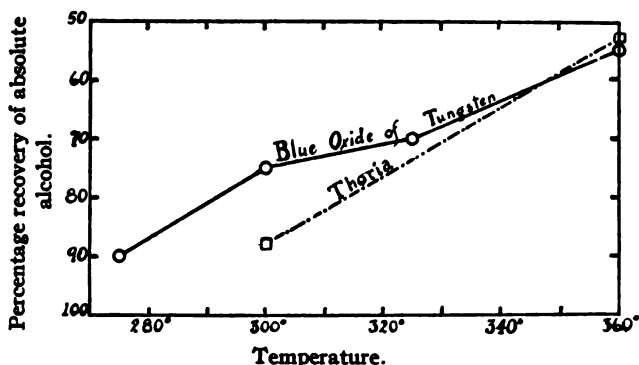


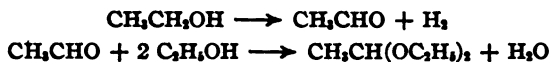
Fig. 3.—Destruction of absolute alcohol.

In operating with any of the above catalysts and ethyl alcohol, the main product of dehydration was ethylene. No trace of ether was detected in any of the experiments, but small traces of other products were found. In almost every instance acetaldehyde was shown to be present. The amounts of this material were quite small at the lower temperatures, but when the temperature reached  $360^{\circ}$ , appreciable amounts were produced by each catalyst, including thorium dioxide, despite the statement of Sabatier that thoria is exclusively a catalyst of dehydration.

It has been stated that no ether was produced in any of the experiments conducted, but in certain cases when thoria or the blue oxide of tungsten was employed, there was produced from alcohol a very small amount of an unidentified liquid boiling between  $30^{\circ}$  and  $40^{\circ}$ . This liquid was lighter than water and immiscible with it. It did not dissolve in alkali, reduce ammoniacal silver solution, interact with phenylhydrazine, nor decolorize bromine water. It burned with a colorless flame, and had a peculiar musty odor.

When operating over thoria at  $325^{\circ}$  in the presence of carbon dioxide, a 2% yield was obtained of a liquid distilling between  $80^{\circ}$  and  $110^{\circ}$ , when the temperature of the furnace was raised to  $425^{\circ}$ , this fraction constituted about 10% of the recovered material, and boiled between  $80^{\circ}$  and  $95^{\circ}$ . It was lighter than water and immiscible with it. Further examination of this material showed it to consist chiefly of acetal, mixed

with unchanged alcohol. The presence of carbon dioxide seemed to promote the formation of this product, which might result from the dehydrogenation of alcohol under the influence of thoria, yielding acetaldehyde, which could then condense with the excess of alcohol. Its complete synthesis may be expressed as follows.



### The Decomposition of Carbon Disulfide

Pure, dry carbon disulfide, when vaporized over pumice or over the blue oxide of tungsten, suffered little or no decomposition. At 400° there was a slight discoloration, due to the formation of a trace of brown, resinous material. When carbon dioxide was passed through the furnace with the carbon disulfide, there was no reaction as long as the gases were perfectly dry. But if moisture was present in any amount, or if the contact mass was not perfectly dry, then hydrogen sulfide was always produced in direct proportion to the amount of water present. It was thought possible that some carbon oxysulfide might be evolved from this reaction, as had been observed by Meyer and Schuster<sup>17</sup> at a higher temperature, but analysis of the gas failed to reveal any such reaction product.

### The Interaction of Ethyl Alcohol and Carbon Disulfide

Absolute alcohol was mixed with purified carbon disulfide in the proportion of two moles of the former to one mole of the latter. When this mixture was passed over pumice at a rate varying between 20 g. and 40 g. per hour, the weight of the recovered liquid varied between 91% and 98% of that employed. In each case, the formation of hydrogen sulfide was observed, but analyses revealed no carbon oxysulfide. The hydrogen sulfide doubtless resulted from the interaction of the carbon disulfide with the small amount of water present in the alcohol. When carbon dioxide was passed through the furnace along with the vapor mixture, it exercised no appreciable influence on the course of the reaction.

When the alcohol-carbon disulfide mixture was passed over Thoria C at 300° the recovered liquid represented 82% of the weight of the original material. At 400° only about 45% was recovered. The evolution of hydrogen sulfide was much greater at the higher temperature, which temperature was also productive of a considerable quantity of ethyl mercaptan, resulting from the condensation of alcohol with the hydrogen sulfide generated. This condensation forms one mole of water, which may again react with more carbon disulfide for the further production of hydrogen sulfide, so that a trace of water in the original alcohol would suffice, theoretically, for the conversion of the entire mixture into car-

<sup>17</sup> Meyer and Schuster, *Ber.*, 44, 1931 (1911).

bon dioxide and ethyl mercaptan. In practice, however, only moderate quantities of mercaptan were obtained.

High-boiling liquids were obtained from this reaction, but in small quantities. Of this product, very little boiled between  $100^{\circ}$  and  $160^{\circ}$ , but the fractions between  $160^{\circ}$  and  $228^{\circ}$  were considerably larger. All fractions were specifically lighter than water in which they were insoluble. The higher fractions were partially or totally insoluble in hydrochloric acid and in potassium hydroxide solution, but soluble in benzene and in alcohol. All possess a very nauseating odor.

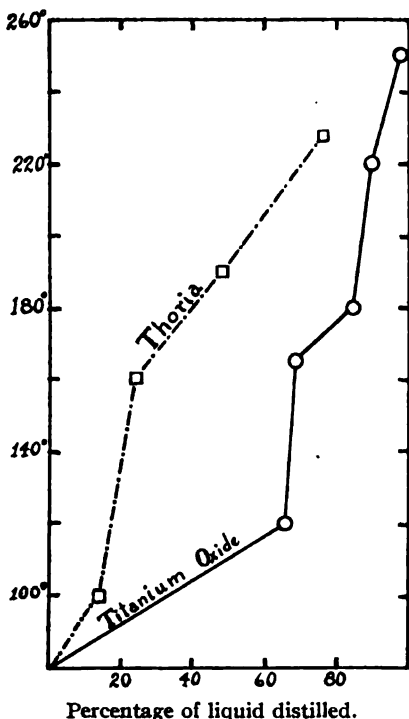


Fig. 4.—Comparative distillation of high-boiling liquids produced by the action of catalysts upon a mixture of alcohol and carbon disulfide.

ing 16% of material boiling within a range of  $15^{\circ}$  between  $165^{\circ}$  and  $180^{\circ}$ ; but as there was only 10 cc. of this liquid, its purification was not attempted. Whether we are dealing here with thiocarbonate combinations remains to be established.

The blue oxide of tungsten shows a very different behavior from that of thoria and titanium oxide. At  $265^{\circ}$  there was very little reaction during vaporization of the mixture of alcohol and carbon disulfide. A small

Titanium oxide, in the light of its inactivity toward ethyl alcohol, gave surprising results when used as a catalytic mass with mixtures of alcohol and carbon disulfide. The rate of passage through the furnace varied between 13 g. and 18 g. of liquid per hour. At  $225^{\circ}$  the liquid recovered represented 94% of the weight of the original amount used. At  $300^{\circ}$  this value dropped to 84%, and at  $355^{\circ}$  and  $360^{\circ}$  the recovery represented 50% and 46%, respectively, of the original weight. Large quantities of hydrogen sulfide were evolved in each experiment and the yield of pure ethyl mercaptan at  $360^{\circ}$  with this catalyst was about 10%.

High-boiling liquids were produced in the presence of this catalyst, similar to those produced with thoria, but the yields were very much smaller. The distillation of fractions above 80% from these two products is shown graphically in Fig. 4. The most promising feature of the titanium

oxide curve is the section representing

amount of hydrogen sulfide was evolved, but the 91% of recovered liquid contained no reaction product that could be isolated. At 300° there was an 89% recovery of liquid, which contained a trace of mercaptan, while a mixture of hydrogen sulfide and ethylene was evolved. When the temperature was raised to 325°, gaseous evolution increased, and the recovered liquid represented 80% of the original weight, and contained only a small amount of mercaptan. At 360° there was vigorous evolution of ethylene and hydrogen sulfide, and 66% by weight of the liquid was recovered. This material separated into two layers, a phenomenon not observed with the other catalysts. This shows the pronounced dehydrating action of this catalyst, in that enough water was produced to throw the carbon disulfide out of the alcoholic solution. Production of mercaptan by this

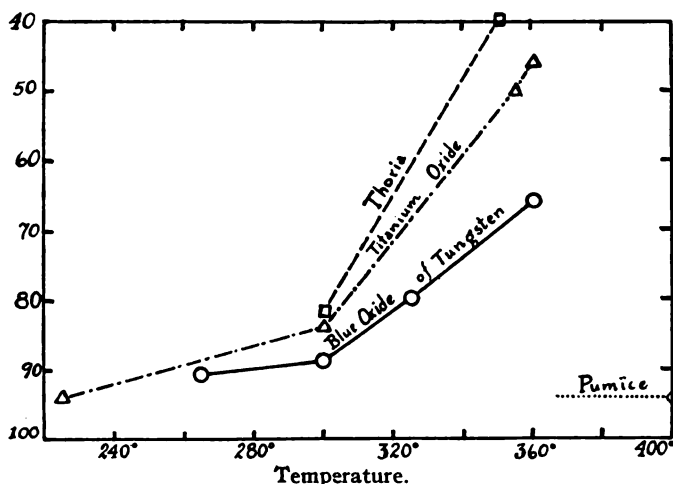
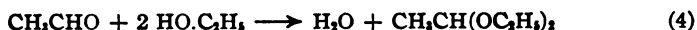
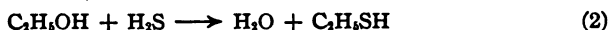
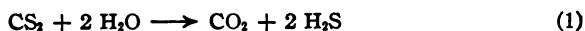


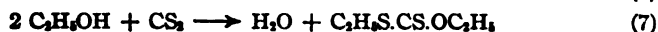
Fig. 5.—Gaseous products of the action of various catalysts upon a mixture of carbon disulfide and ethyl alcohol.

catalyst was far inferior to that by thoria and titanium oxide, but the ethylene production was much greater. The presence of carbon dioxide seemed to exert no influence on the course of the reaction.

Comparison of the activity of these four contact catalysts is not an easy matter. It has been however, shown that the following 5 reactions occur.



There are also numerous other possible reactions, including the formation of thio-esters, as indicated in the following equations.



In Fig. 5 is shown the production of gas from mixtures of alcohol and carbon disulfide passing over catalysts at various temperatures. (Equations 1, 3, 5). Pumice, as would be expected, is quite inert; but titanium dioxide, which has been shown to exert almost no catalytic influence on ethyl alcohol alone (Equations 3 and 5), shows the formation of a large amount of volatile products. This may be due, then, to the formation of hydrogen sulfide (Equation 1), which supposition is confirmed by the relatively large production of mercaptan, as shown in Equation 2.

The blue oxide of tungsten has been shown to be a much more active dehydrating agent toward ethyl alcohol alone than the other catalysts employed, and yet the amount of volatile products from the mixture is, according to Fig. 5, much less than was produced by thoria or by titanium oxide. This fact would indicate that the blue oxide of tungsten functioned in a series of reactions which produced a maximum of water and a minimum of gaseous products. Or it may be possible that a reaction occurred between these gaseous products, whereby they were transformed into non-volatile compounds. Whether or not any ethyl esters of carbon disulfide were formed, as indicated in Equations 6 and 7, was not proved. A small amount of high-boiling material was found in almost every experiment, but a sufficient quantity of this material was never obtained to permit the isolation of any pure compound.

### Summary

1. Alcohol vapors alone, or in the presence of carbon dioxide, may be passed over pumice at 500° without undergoing appreciable decomposition.
2. By strongly calcining thoria, or by prolonged heating at a lower temperature, this oxide may be inactivated for dehydration of ethyl alcohol.
3. Thoria is not exclusively dehydrating in its action upon ethyl alcohol. Under certain conditions a considerable amount of aldehyde is produced by dehydrogenation.
4. The titanium oxide employed as a catalyst effected practically no dehydration of ethyl alcohol at temperatures up to 355°.
5. The blue oxide of tungsten at lower temperatures is a much more active catalyst for the production of ethylene than is thoria, but at higher temperatures they are practically of equal efficiency.
6. No ether was produced from alcohol in the presence of any of the catalysts.
7. By operating over thoria in the presence of carbon dioxide, a considerable quantity of acetal was formed from ethyl alcohol.
8. Pure, dry carbon disulfide, when vaporized over pumice or over the

blue oxide of tungsten, suffers no decomposition at temperatures up to 400°. A trace of moisture, however, causes decomposition and the evolution of hydrogen sulfide.

9. In the presence of any of the three metallic oxides employed as catalysts, a mixture of absolute alcohol and carbon disulfide produced considerable quantities of ethyl mercaptan. Titanium dioxide, which had been almost without action upon alcohol alone, proved the most active catalyst for this esterification. This new method may be advantageous for the synthesis of certain mercaptans.

10. From alcohol and carbon disulfide, amounts of high-boiling liquids were obtained, but in quantities too small for identification. We obtained no other evidence of the formation of esters of thiocarbonic acids by interaction of alcohol and carbon disulfide.

NEW HAVEN, CONNECTICUT

[ CONTRIBUTION FROM THE BUREAU OF STANDARDS OF THE DEPARTMENT OF COMMERCE ]

## ABIETIC ACID AND CERTAIN METAL ABIETATES<sup>1</sup>

BY LAWRENCE L. STEELE

Received February 3, 1922

### Introduction

Abietic acid is the name most commonly given to the crystalline material made by treating ordinary rosin with alcohol or other organic solvents. Many years ago Maly<sup>2</sup> expressed the view that rosin was essentially the anhydride of abietic acid, but his idea has not been generally accepted. Recently Knecht and Hibbert<sup>3</sup> have presented strong evidence in favor of the anhydride theory for rosin. From the assumption that rosin is an acid anhydride, a new method for the preparation of abietic acid has been developed by which a pure product can be made more easily and in larger yield than by the older published methods. Some physical and chemical data of the product will be given together with a description of the preparation of several metallic abietates with their analyses for metal content.

### Methods for the Preparation of Abietic Acid

The method of Maly<sup>4</sup> has been used extensively for preparing abietic acid. Rosin is heated with 70% alcohol, whereby after some hours it partly dissolves and partly crystallizes. The impure crystals are treated in the same way with dil. alcohol a number of times and finally repeatedly recrystallized from strong alcohol. The method is tedious and the yield of pure product is very low.

<sup>1</sup> Published by permission of the Director of the Bureau of Standards.

<sup>2</sup> Maly, *Ann.*, 149, 244 (1869).

<sup>3</sup> Knecht and Hibbert, *J. Soc. Dyers Colour.*, 35, 150 (1919).

<sup>4</sup> Maly, *J. prakt. Chem.*, 86, 111 (1862).

Levy<sup>5</sup> fractionally distilled rosin in a vacuum and crystallized the distillate from methyl alcohol. The product melted at 178–182° and was probably an isomer of the acid prepared from rosin without distillation.

Cohn<sup>6</sup> heated powdered white rosin with methyl alcohol and a small proportion of strong sulfuric acid. The mixture partly solidifies to an impure crystal mass of abietic acid which is washed and recrystallized from pure methyl alcohol. The product by this method is liable to be contaminated with a yellow impurity, hard to remove, probably formed by the action of the sulfuric acid upon impurities in the rosin.

Knecht and Hibbert<sup>7</sup> dissolved rosin in glacial acetic acid and allowed the solution to stand for a week, whereby abietic acid separated and was filtered off and recrystallized approximately 20 times from acetic acid, methyl alcohol and ethyl alcohol. This method is tedious and the yield of pure product is low.

### Description of a New Method for the Preparation of Abietic Acid

If the view that rosin contains abietic anhydride is accepted, it follows that in all the methods for the isolation of abietic acid from rosin, the process is essentially one of hydration. The fact that rosin is hydrated by a solvent containing water was proved by the following experiments. In 2 flasks equal weights of rosin were dissolved by heating in approximately the same weight of 98% acetic acid. One flask was then set aside while the contents of the other flask were boiled vigorously under a reflux condenser for 2 hours. The contents of both flasks were then brought to room temperature and a few crystals of abietic acid added to each flask. In a short time crystallization started in the flask which had been heated for the period of 2 hours and after several hours this flask was nearly filled with crystals. The contents of the other flask did not crystallize to an appreciable extent, even after standing for 3 days. It was evident that the rosin was hydrated by heating with the 98% acetic acid. The following method for the preparation of abietic acid from rosin was developed after a series of experiments.

Seven hundred g. of white rosin (WW or WG grade) in small lumps<sup>8</sup> was boiled with 500 cc. of 98% acetic acid for 2 hours under a reflux condenser. The mixture was then filtered while hot through a large plaited filter paper and the filtrate cooled to room temperature or lower. A few crystals of abietic acid were added to start crystallization or, when none of this product was available, the solution was allowed to stand overnight, this whereby spontaneous crystallization took place. If the solution was "seeded" with abietic acid, it usually started to crystallize within an hour and the liquid became a solid mass of crystals after standing overnight. The product was filtered on a Büchner funnel with suction and the filtrate set aside for a second crop of crystals. The material on the filter was

<sup>5</sup> Levy, *Z. anorg. Chem.*, **18**, 1739 (1905).

<sup>6</sup> Cohn, *Chem. Ztg.*, **40**, 791 (1916).

<sup>7</sup> Ref. 3, p 151.

<sup>8</sup> Rosin which has stood in powdered form for considerable lengths of time becomes partially oxidized and is unsuitable.

sucked as free from mother liquor as possible and washed with successive portions of cold alcohol (9 parts by volume of 95% ethyl or denatured alcohol to one part of water) until the filtrate was practically colorless.

The yield of air-dried product was usually about 350 g., counting the second crop of material recovered from the mother liquor. Some of the product, prepared as above, was placed on a bit of porous porcelain plate and washed with a little strong alcohol. This material when dried and powdered showed a melting point of 155–159°. Some of the product was recrystallized from 95% alcohol and then was found to melt at 158–162°. These crystals had been washed thoroughly with the dil. alcohol and dried in a vacuum before the melting-point determination was made. A material of melting point 161–165° resulted from a second crystallization in the same manner, while after a third crystallization, the product was unchanged in melting point.<sup>9</sup>

The melting-point determinations were made with a totally immersed calibrated thermometer by the common capillary-tube method. A rate of heating of approximately 1° rise per minute was used, the sample being introduced into the bath at a temperature of 150°.

Glacial acetic acid (98%) was found to be more efficient than alcohol for recrystallizing impure abietic acid. For example, 100 g. of the crude acid was dissolved by heating in 100 cc. of acetic acid and filtered while hot to remove suspended matter. The filtrate was cooled and constantly stirred, whereby a fine crystal meal was deposited. This product was filtered with suction and washed with the wash alcohol described above until the washings were practically colorless. The yield of material in this crystallization was approximately 80 g., which was considerably higher than the yield from 98% alcohol.

### Physical and Chemical Data of the Abietic Acid Prepared by the New Method

**Crystallographic Measurements.**—Through the kindness of Dr. H. E. Merwin of the Geophysical Laboratory of the Carnegie Institution of Washington, crystallographic measurements of some crystals of abietic acid from alcohol were made and reported as follows.

"The crystals are sharply-bounded, three-sided tables with angles of approximately 45° and 90°. Most faces of 6 that were measured showed only fair or poor reflections, but identity with abietic acid as described by Graber was established with regard to habit and angles and also optical properties (as below). An unlisted form  $\bar{1}01$  having small faces and giving good reflections was observed. The form  $m(110)$  was represented by small rough faces. The measurements are summarized thus:  $a(100)\Delta\mu(1\bar{1}0) = 47^\circ 29'$ ;  $a(100)\Delta c(001) = 68^\circ 22'$ ;  $c(001)\Delta(\bar{1}01) = 48^\circ 1'$  (calculated  $48^\circ 29'$ );  $a(100)\Delta\omega(\bar{1}11) = 70^\circ 7'$ .

<sup>9</sup> There is good evidence that abietic acid commences to form anhydride at temperatures near its melting point and hence the observed melting point is not sharp.



Under the microscope, tables lying flat on (100) show the plane of the optic axes parallel to the long edge, therefore to (010); the obtuse bisectrix,  $\gamma$ , emerges about  $15^\circ$  from the center of the field; tables standing vertical, resting on the long edge, extinguish at  $13^\circ$  or  $14^\circ$ , and  $\alpha$  is in acute angle  $\beta$ . The refractive indices, measured by means of the petrographic microscope with a probable error not exceeding  $\pm 0.003$ , are:  $\alpha = 1.510$ ,  $\beta = 1.578$ ,  $\gamma = 1.618$ . These were not previously known."

**Optical Rotation Measurements.**—Through the kindness of Mr. C. F. Snyder of the Sugar Laboratory, Bureau of Standards, a measurement of the optical rotatory power of a sample of abietic acid thrice crystallized from alcohol, was made in alcoholic solution. Approximately 10 g. of the acid in 100 cc. of absolute ethyl alcohol gave a reading of  $[\alpha]_D^{20} = -80.0^\circ$ . This value agrees closely with the rotation measurement of  $[\alpha] -77.9^\circ$  reported by Schulz<sup>10</sup> on a sample of abietic acid prepared by treating American rosin in alcoholic solution with hydrochloric acid.

**Iodine Value by the Wijs Method.**—The Wijs iodine number was determined upon a sample of abietic acid thrice crystallized from alcohol and dried in a vacuum. The Wijs solution was prepared as in the standard method for the determination of the iodine number of shellac. Samples weighing approximately 0.2 g., dissolved in 10 cc. of chloroform, were mixed with 25 cc. of the Wijs solution and the reaction allowed to run for one-half hour in the dark at different temperatures.

At  $0^\circ$  the iodine value was 153.2, 152.7; at  $22-23^\circ$ , 166.8, 169.3; and at  $25-26^\circ$ , it was 168.5, 171.1.

The theoretical iodine value for abietic acid, assuming the presence of two double bonds, is 167.9. Abietic acid appears to require very nearly two molecules of halogen for saturation.

**Acid Value.**—The acid number of a sample of abietic acid (melting point  $161-165^\circ$ ) was determined by titration in alcoholic solution with standard alkali, using phenolphthalein as an indicator; 1.336 g. of material required 19.6 cc. of alkali (1 cc. = 0.01265 g. of potassium hydroxide) corresponding to an acid number of 186. The theoretical acid number for a monobasic acid of formula  $C_{20}H_{30}O_2$  is 185.6.

### Study of Certain Metallic Abietates

**Discussion of Metallic Abietates.**—Manganese and cobalt resينات, made by adding a solution of a salt of one of these metals to a solution of the sodium soap of rosin, are important commercial products used as driers in paint oils and varnishes. Ellingson<sup>11</sup> in 1914 prepared a number of metallic derivatives of abietic acid and reported that in nearly every case the metallic abietates were acid salts. For example, he found the metal content of the manganese derivative to be 4.92%, while the normal

<sup>10</sup> Schulz, *Chem. Ztg.*, 41, 666 (1917).

<sup>11</sup> Ellingson, *THIS JOURNAL*, 36, 325 (1914).

salt should contain 8.35%. The cobalt derivative was likewise reported to contain a very much lower percentage of metal than the theoretical content of the normal salt. On the other hand, there are commercial manganese and cobalt salts of rosin sold, with an advertised metal content in each case, which corresponds more closely to a normal salt.

A study of the abietates of lead, manganese, cobalt, nickel, iron and chromium was made, in order to settle the question whether these salts are normal, acid or basic in character.

### Preparation and Analysis of Metallic Abietates

Metallic abietates were prepared from abietic acid by the following general procedure.

Freshly recrystallized acid was dissolved in about 10 times its weight of denatured alcohol and nearly neutralized by the addition of a calculated amount of strong sodium hydroxide solution of known strength. The solution was then titrated to a faint pink color with dil. alcoholic sodium hydroxide solution, using phenolphthalein as an indicator. This neutral abietate solution was then poured slowly, with stirring, into a solution of a salt of the desired metal dissolved in 40 to 50 times its weight of distilled water. A 50% excess of the metallic salt was used in order to ensure complete precipitation of the abietate. The resulting soap was thrown down as an amorphous, more or less flocculent precipitate, which was filtered on a Büchner funnel and washed thoroughly with water until free from soluble material. In cases where the product formed a gelatinous cake on the filter, it was found advantageous to transfer it to a dish and churn it with water. This mixture was then filtered again on the same funnel.

The thoroughly washed product was dried in small portions in a vacuum in order to avoid oxidation. The wet precipitate was placed in a heavy-walled test-tube and connected with an oil vacuum pump, with a drying tower of fused calcium chloride between the tube and the pump. In order to hasten the drying, the tube was placed in a water-bath at 80–90°, whereby the greater part of the moisture was rapidly removed. The last traces of water were held rather tenaciously by the metallic soap and several hours were found to be necessary for complete drying of the product.

When the metallic abietates had been partially dried, the vaporization of the remaining moisture caused the particles to fly about violently, and a wad of absorbent cotton was necessary in the mouth of the tube to prevent loss.

In case there were large aggregates of material formed, they were broken up with a spatula and the drying then continued. When the abietates were dry there was no further flying of particles observed, upon shaking the evacuated and heated tube. The dried metallic soaps were somewhat

hygroscopic and slowly absorbed oxygen from the air, especially in the case of the manganese and cobalt derivatives. For this reason the dried products were either kept in an evacuated tube or used promptly.

A description of the preparation of the individual abietates, with analyses for their metal content, follows.

**Lead Abietate.**—Lead abietate was prepared from sodium abietate and c. p. reagent lead nitrate. The product was pure white when fresh, but changed to a light yellow on continued exposure to air for several weeks. It was analyzed by decomposing a weighed sample in a Kjeldahl flask with sulfuric acid, using small quantities of nitric acid to oxidize organic matter. The nitric acid was subsequently removed through dilution with water and heating until the sulfuric acid reached the fuming point. The lead was determined as sulfate by the standard method.

*Analyses.* Calc. for  $\text{Pb}(\text{C}_{20}\text{H}_{31}\text{O}_2)_2$ : Pb, 25.59. Found: 24.69, 24.71.

Approximately 1.5 g. of lead abietate was ashed at low temperature in a nickel crucible, the ash extracted with distilled water and the mixture filtered. The filtrate was found to be alkaline with phenolphthalein as an indicator and when titrated hot with 0.05 *N* sulfuric acid, required 0.27 cc. for neutralization. This corresponded to nearly 0.5 mg. of sodium hydroxide, equivalent to 4.4 mg. of sodium abietate. It was apparent that the lead abietate contained approximately 0.25% of sodium abietate, possibly in an included form in the precipitate.

**Manganese Abietate.**—Manganese abietate was prepared from sodium abietate and c. p. reagent manganese sulfate. The freshly precipitated product was white with a pinkish tinge, while the material after drying was a light flesh color. It was analyzed for metal content by ashing a 0.5-g. sample in a porcelain crucible, dissolving the ash in mineral acid, and titrating the manganese by the standard bismuthate method.

*Analyses.* Calc. for  $\text{Mn}(\text{C}_{20}\text{H}_{31}\text{O}_2)_2$ : Mn, 8.35. Found: 8.17, 8.20.

Approximately 0.7 g. of manganese abietate was ashed at low temperature in a nickel crucible, the ash extracted with distilled water and the mixture filtered. The filtrate gave no color with phenolphthalein, which indicated that the manganese soap contained no appreciable amount of sodium abietate as an impurity.

**Cobalt Abietate.**—Cobalt abietate was prepared from sodium abietate and c. p. reagent cobalt chloride (labeled to contain only 0.18% nickel). The wet material was a deep lavender color, while the dried abietate was pale lavender, which turned to a dirty gray after an exposure of several days to the air. This change was due to oxidation: for example, approximately 0.9 g. of the product gained in weight 9 mg. during an exposure to air on the steam-bath for one hour.

Cobalt abietate was analyzed for metal content by ashing a 1-g. sample in a porcelain crucible, dissolving the ash in mineral acid and determining cobalt in the solution as metal by electrolysis.

*Analyses.* Calc. for  $\text{Co}(\text{C}_{20}\text{H}_{31}\text{O}_2)_2$ : Co, 8.91. Found: 8.44, 8.46.

Approximately 0.6 g. of cobalt abietate was ashed at low temperature in a nickel crucible, the ash extracted with distilled water and the mixture filtered. The filtrate reacted alkaline to phenolphthalein and required three drops of 0.05 normal acid for neutralization. It was evident that the cobalt abietate contained only a trace of sodium abietate as an impurity.

**Nickel Abietate.**—Nickel abietate was prepared from sodium abietate and c. p. reagent nickel chloride (labeled to contain a "trace" of cobalt). The dried product was light green and did not alter visibly on exposure to air. It was analyzed for metal content by decomposing a 1.5-g. sample in a Kjeldahl flask with sulfuric-nitric acid mix-

ture and precipitating nickel in the resulting solution by the glyoxime method. Another sample was ashed in a porcelain crucible, the ash dissolved in mineral acid, and the nickel determined by electrolysis.

*Analyses.* Calc. for  $\text{Ni}(\text{C}_{20}\text{H}_{39}\text{O}_2)_2$ : Ni, 8.87. Found: glyoxime method, 7.68, 7.69; by electrolysis, 7.67.

Another sample of nickel abietate was prepared from sodium abietate and c. p. nickel acetate (containing 0.07% of cobalt). Analyses was made by ashing a sample in a porcelain crucible, dissolving the ash in mineral acid and determining nickel by the glyoxime method.

*Analyses.* Found: Ni, 8.04, 8.13.

Approximately 0.9 g. of nickel abietate was ashed at low temperature in a nickel crucible, the ash extracted with distilled water and the mixture filtered. The filtrate was alkaline to phenolphthalein and when titrated hot with 0.05 *N* sulfuric acid, required 0.88 cc. for neutralization. This corresponded to nearly 1.75 mg. of sodium hydroxide, equivalent to 14.2 mg. of sodium abietate. It was evident that the nickel abietate contained approximately 1.6% of sodium abietate as an impurity.

**Chromium Abietate.**—Chromium abietate was prepared from sodium abietate and c. p. reagent chromium potassium sulfate. The dried product was a dirty green and was analyzed for metal content by ashing a sample in a porcelain crucible, effecting solution of the chromic oxide by a fusion method, and determining chromium by an electrometric titration.

*Analyses.* Calc. for  $\text{Cr}(\text{C}_{20}\text{H}_{39}\text{O}_2)_2$ : Cr, 5.44. Found: 1.97, 2.03.

**Iron Abietate.**—Iron abietate was prepared from sodium abietate and c. p. reagent ferric alum. The dried product was light brown and was analyzed for metal content by ashing a sample in a porcelain crucible, effecting solution of the ferric oxide by a fusion method, and titrating the iron by the standard permanganate method. Another sample was precipitated as hydroxide and ignited to oxide.

*Analyses.* Calc. for  $\text{Fe}(\text{C}_{20}\text{H}_{39}\text{O}_2)_2$ : Fe, 5.82. Found: 2.44, 2.59, 2.41.

Approximately 1 g. of iron abietate was ashed in a nickel crucible, the ash extracted with water and the mixture filtered. The filtrate was alkaline to phenolphthalein and required 0.55 cc. of 0.502 *N* acid for neutralization, corresponding to 0.011 g. of sodium hydroxide or 0.0894 g. of sodium abietate. It was evident that the iron abietate contained approximately 9% of sodium abietate as an impurity.

The conclusion was drawn that neither the iron nor the chromium abietate corresponds to a normal salt, but that they both contain an excess of abietic acid. It is well known that aqueous solutions of chromium and ferric iron are hydrolyzed and hence show an appreciable hydrogen-ion concentration. It is probable that when a neutral solution of sodium abietate is added to a chromium or iron solution, a combination of some abietate and hydrogen ions takes place with the formation of insoluble abietic acid, while a corresponding amount of metallic hydroxide forms. If this latter is in a colloidal condition, it may be subsequently removed during the washing of the precipitate. At the same time there may be the usual combination of iron or chromium ions with abietate ions to form the insoluble metallic abietates, so that the final product may be essentially a mechanical mixture of abietic acid and ferric or chromium abietate, contaminated with small amounts of sodium abietate.

The preparation of iron and chromium abietate in an organic medium was attempted in the hope that here a normal salt would result. Ferric chloride was dissolved in 95% alcohol and the solution added slowly to a neutral alcoholic solution of sodium abietate until no further precipitate was formed. The buff colored product was filtered on a Büchner funnel with suction and washed with alcohol until free from ferric chloride.

The dried product was analyzed for metal content by ashing a sample in a porcelain crucible, dissolving the ferric oxide in mineral acid, and titrating iron by the standard permanganate method.

*Analyses.* Calc. for  $\text{Fe}(\text{C}_{20}\text{H}_{39}\text{O}_2)_2$ : Fe, 5.82. Calc. for  $\text{Fe}(\text{OH})(\text{C}_{20}\text{H}_{39}\text{O}_2)_2$ : Fe, 8.27. Found: 7.25, 7.23.

The product was completely soluble in cold benzene and in cold raw linseed oil, giving a deep red solution in each case. Another lot of the same material prepared in an identical manner showed on analysis an iron content of 7.69%.

The conclusion can be drawn that a basic ferric abietate of indefinite formula was formed by the interaction of ferric chloride and sodium abietate in alcoholic solution.

A solution of chromium chloride in 95% alcohol was added slowly to an alcoholic solution of sodium abietate until there was no further formation of precipitate. The product was filtered with suction, washed with alcohol and then with water, and dried in a vacuum. The bluish-green product was analyzed for metal content by ashing in a porcelain crucible, fusing the chromic oxide with sodium peroxide and titrating the chromate by the regular dichromate method.

*Analyses.* Calc. for  $\text{Cr}(\text{C}_{20}\text{H}_{39}\text{O}_2)_2$ : Cr, 5.44. Calc. for  $\text{Cr}(\text{OH})_2(\text{C}_{20}\text{H}_{39}\text{O}_2)_2$ : Cr, 13.42. Found: 14.93, 15.16.

The product was found to be practically insoluble in benzene. The conclusion can be drawn that a basic chromium abietate, containing at least two hydroxyl groups, was formed by the interaction of chromium chloride and sodium abietate in alcoholic solution.

### Discussion of Results

It was found that all of the metallic abietates described above were soluble in benzene (with the exception already noted of the basic chromium salt). This fact would indicate the absence of any appreciable amount of metallic hydroxide in the products. The metallic content found for the manganese and cobalt abietates corresponded closely to that of the normal salt. The lead and nickel derivatives were only slightly lower in metal content than required for the corresponding normal salts. The nickel abietate precipitated from nickel acetate solution was slightly higher in metal content than the material precipitated from nickel chloride solution. Possibly there may have been more hydrolysis in the case of the chloride than in the case of the acetate.

The iron and chromium abietates prepared in aqueous solution contain an excess of abietic acid. A possible reason for this has already been discussed.

The attempt to prepare normal abietates of iron and chromium by precipitation in alcoholic solution resulted in the formation of strongly basic salts of more or less indefinite composition.

### Summary

1. A new method for the preparation of abietic acid from rosin is described, and physical and chemical data of the product are given.
2. Certain metallic derivatives of abietic acid are discussed and a de-

scription is given of the preparation of lead, manganese, cobalt, nickel, iron and chromium abietates from pure abietic acid.

Acknowledgment is made to Messrs. Bright, Hickson and Scherrer of the Bureau staff for their assistance in the analysis of the metallic abietates.

WASHINGTON, D. C.

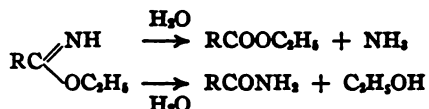
[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, YALE UNIVERSITY]

## THE SPONTANEOUS DECOMPOSITION OF IMIDO ESTERS

By TREAT B. JOHNSON AND LAWRENCE W. BASS

Received March 4, 1922

It is well known that imido esters are extremely susceptible to hydrolytic change with formation of the corresponding oxygen esters or acid amides respectively, and that they cannot be distilled at ordinary pressure



without undergoing dissociation into a nitrile and alcohol. This dissociation has also been observed to take place at ordinary temperature, and it



seems to be quite characteristic<sup>1</sup> also for the transformation to proceed beyond the nitrile stage and as a final result for the latter to undergo almost complete polymerization to its trimolecular form. In fact, Pinner<sup>2</sup> recommends as the best method of preparing cyaphenine ( $\text{C}_6\text{H}_5\text{CN}$ ), to allow crude undistilled benzimido-ethylether to undergo spontaneous decomposition at ordinary temperature. Wheeler, Walden and Metcalf<sup>3</sup> state that pure benzimido-methylether can be kept for months without change.

A most interesting and striking fact in connection with these dissociations is the pronounced tendency for the nitriles to undergo polymerization. Ordinarily these compounds, when free from impurities, are not characterized by their instability, and where polymerization has been observed it has quite generally been induced by the action of a variety of polymerizing reagents such as sulfuric acid, metallic sodium, and aluminum chloride, or by heating at high temperatures.<sup>4</sup>

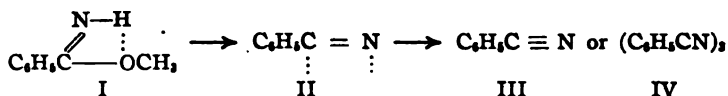
<sup>1</sup> Glock, *Ber.*, 21, 2652 (1888).

<sup>2</sup> Pinner, *ibid.*, 22, 1611 (1889).

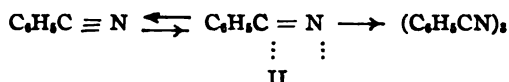
<sup>3</sup> Wheeler, Walden and Metcalf, *Am. Chem. J.*, 20, 68 (1898).

<sup>4</sup> Pinner and Klein, *Ber.*, 11, 764 (1878). Lottermoser, *J. prakt. Chem.*, [2] 54, 1331 (1901). Frankland and Evans, *J. Chem. Soc.*, 37, 563 (1880). Eitner and Kraft, *Ber.*, 25, 2267 (1892). Scholl and Noir, *ibid.*, 33, 1055 (1900). Meyer and Nabe, *J. prakt. Chem.*, [2] 82, 536 (1910). Francis and Davis, *J. Chem. Soc.*, 83, 259 (1904).

In imido ester decompositions we have only one dissociation product to influence the polymerization, namely, alcohol; therefore in such cases one might explain the tendency to polymerize as being due to the unsaturated condition of the nitrile at the moment of dissociation of the imido-ester molecule. This unsaturation may be expressed as follows.



In other words, polymerization to cyaphenine IV takes place before the free valences of the unsaturated cyanide group II have readjusted themselves into the stable condition of the nitrile molecule III. Both changes—formation of nitrile and polymerized nitrile—are therefore to be expected in imido ester decompositions at ordinary temperature. The rearrangement of ordinary benzonitrile into cyaphenine under the influence of polymerizing agents may also be interpreted as a case of disturbance of valence equilibrium in the nitrile by the catalyst, giving the unstable form II which then immediately polymerizes to a cyclic compound.



We are now able to record the results of a series of experiments which add further interest to this subject. In order to gain further data regarding the stability of imido ester combinations and the tendency for nitriles to polymerize to cyaphenines, Professor Henry L. Wheeler and T. B. Johnson in 1900 prepared fresh samples of benzonitrile and the following imido esters, namely, benzimido-methylester, benzimido-ethylester, benzimido-*isobutylester*, and *p*-tolylimido-methylester. They purified them very carefully by distillation under diminished pressure and then sealed them in glass containers and set them aside for future observation. These samples were examined by the writers in February, 1922, or after a period of storage covering 22 years. In every case, with the exception of the specimen of benzonitrile, we found heavy crystalline deposits of cyaphenine combinations and also unaltered nitrile. The pure benzonitrile showed no evidence of polymerization and the same behavior was also exhibited by *p*-tolynitrile which has been preserved in our cabinet for several years. In the case of benzimido-methylester this reagent had undergone practically complete decomposition and very little nitrile was present. The cyaphenine had deposited in beautiful prismatic crystals, some of which were over 2 cm. in length. They melted sharply without further purification at 229–230°.

The benzimido-*isobutylester* and the corresponding ethylester had not undergone complete dissociation. Benzonitrile and its polymer were

present in both cases, the latter having deposited in glistening prisms melting at 229–230°. From tolylimido-methylester we obtained almost a complete conversion into the polymerized tolylnitrile. This compound (cyantoline)<sup>5</sup> which is recorded in the literature as crystallizing in needles, had deposited in the form of transparent tabular crystals which melted at the correct temperature, 277°, without further purification. Needles were also observed suspended in the remaining oil but the quantity was too small for ascertaining their melting point.

At what time the decomposition of these esters became apparent we have no reliable data, but it is evident from our observations that imido esters of the type examined are not organic combinations which can be preserved for long periods. It is also an extremely interesting fact that polymerization of the nitrile took place in the case of each imido ester, while the pure nitrile remained unchanged during this same period. These results are in accord with the assumption that dissociation of the imido ester leads to the formation of a labile nitrile containing free or residual valences, which rearranges to the stable nitrile and also polymerizes to cyclic derivatives.

NEW HAVEN, CONNECTICUT

[CONTRIBUTION FROM THE MELLON INSTITUTE OF INDUSTRIAL RESEARCH, UNIVERSITY OF PITTSBURGH]

## THE STRUCTURE OF ELASTIC GELS<sup>1</sup>

BY ROBERT HERMAN BOGUE<sup>2</sup>

### Introduction

Received March 22, 1922

The structure of gels is a problem which has occupied the attention of physical chemists since the inception of colloid chemistry, and even before Graham had introduced the distinction between colloid and crystalloid.

Frankenheim<sup>3</sup> in 1835 and von Nägeli<sup>4</sup> in 1858 concluded that jellies were 2-phased and that the solid phase was crystalline. This view has been supported by von Weimarn<sup>5</sup> and Levites,<sup>6</sup> and is at present championed by Bradford.<sup>7</sup>

<sup>1</sup> *Ber.*, 33, 1055 (1900).

<sup>2</sup> Presented before the Pittsburgh Section of the American Chemical Society, March 18, 1922.

<sup>3</sup> Industrial Fellow of the Mellon Institute of Industrial Research of Pittsburgh, and Research Chemist for Armour and Company, of Chicago.

<sup>4</sup> Frankenheim, "Die Lehre von der Kohäsion," Breslau, 1835.

<sup>5</sup> von Nägeli, "Pflanzenphysiologischen Untersuchungen," Zürich, 1858.

<sup>6</sup> von Weimarn, *Kolloid-Z.*, 2, 76, 230, 275, 301, 326 (1908).

<sup>7</sup> Levites, *ibid.*, 2, 161, 208, 237 (1908).

<sup>8</sup> Bradford, The "Physics and Chemistry of Colloids, and Their Bearing on Industrial Questions." Report of a General Discussion held jointly by the Faraday and Physical Societies of London, October 25, 1920. H. M. Stationery Office, London, 1921, p. 44.



Bütschli<sup>8</sup> introduced the idea that there were definite pores in a jelly, and van Bemmelen<sup>9</sup> extended this conception to the postulation of a "cell-like structure of definite form—hanging together at certain points, forming a network." This idea of a network structure in gels has been adhered to by many investigators, but from somewhat variant points of view. Hardy<sup>10</sup> concludes from a microscopical study that the solid phase consists of a solid solution of water in gelatin, and the liquid phase a solution of gelatin in water, and that gelation consists in the separation of the sol into a solid open framework with an interstitial fluid phase. This idea is accepted by Freundlich<sup>11</sup> and Anderson,<sup>12</sup> and in essential respects by Miss Lloyd<sup>13</sup> and Fischer.<sup>14</sup> Wo. Ostwald<sup>15</sup> injected the conception of a 2-phase liquid-liquid system, and Bancroft<sup>16</sup> has adhered to this idea.

Procter<sup>17</sup> has discarded the 2-phase theory of gel structure and postulated the existence of a solid solution of the exterior liquid in the colloid in which both constituents are within the range of the molecular attractions of the mass. This theory was the result of his findings that in a gelatin:acid:water system equilibrium resulted from the combination of the gelatin and acid to form easily dissociated salts, and that the osmotic pressure of these salts and the Donnan equilibrium determined the volume of a swollen jelly. Loeb<sup>18</sup> has carried the idea of Procter to a further explanation of colloidal behavior as described later.

These three schools of thought upon colloid structure represent the present status of the problem. For purposes of classification, although not strictly correct, they may be referred to as the crystalline theory, the colloid theory, and the molecular theory, respectively.

The concept of a crystalline structure in gels has been studied by Scherrer<sup>19</sup> who has made many examinations of gels by means of the Röntgen photograph. He found that certain rigid gels as silicic and stannic acids exhibited well-marked crystalline interference figures in addition to the characteristics of amorphous substances, but in the gel of gelatin the crystalline interference figures were entirely lacking. These different types of gels possess other characteristic dissimilarities. The gel of silicic acid, for example, develops on drying pores that are filled with air, and which may be filled by imbibition with a liquid other than the original solvent.<sup>20</sup> The elastic gels such as gelatin do not develop such pores, and the dried gel will not imbibe a foreign liquid, as, for example, benzene. Harrison<sup>21</sup> has even succeeded in obtaining spherical coagulation-forms of starch which strongly resemble the so-called spherites that were obtained by Bradford from gelatin, but these are not regarded as crystalline.

<sup>8</sup> Bütschli, "Untersuchungen über Structuren," Leipzig, 1898.

<sup>9</sup> von Bemmelen, *Z. anorg. Chem.*, **18**, 14 (1898).

<sup>10</sup> Hardy, *Proc. Roy. Soc.*, **66**, 95 (1900).

<sup>11</sup> Freundlich, "Kapillarchemie," Akademische Verlagsgesellschaft m. b. H., Leipzig, 1909.

<sup>12</sup> Anderson, *Z. physik. Chem.*, **88**, 191 (1914).

<sup>13</sup> Lloyd, *Biochem. J.*, **14**, 147 (1920).

<sup>14</sup> Fischer, "Soaps and Proteins," John Wiley and Sons, New York, 1921.

<sup>15</sup> Wo. Ostwald, *Arch. ges. Physiol.* (Pfüger's), **109**, 277 (1905); **111**, 581 (1906).

<sup>16</sup> Bancroft, "Applied Colloid Chemistry," McGraw-Hill Co., New York, 1921, pp. 239, 242.

<sup>17</sup> Procter, *J. Chem. Soc.*, **105**, 313 (1914).

<sup>18</sup> Loeb, *J. Gen. Physiol.*, **3**, 827 (1921); **4**, 73, 97, 351 (1921-22).

<sup>19</sup> Scherrer, *Machr. Ges. Wiss. Göttingen*, 1918, p. 96.

<sup>20</sup> Hatschek, Ref. 7, p. 59.

<sup>21</sup> Harrison, *J. Soc. Dyers Colourists*, **32**, 32 (1916).

It seems probable from the differentiation found between silicic acid and gelatin gels that, as Hatschek has observed, there are many kinds of structure in gels. In the present paper we shall concern ourselves only with the elastic gels. The theory of Procter, while explaining adequately the swelling phenomena of gelatin, does not account for other colloidal behavior, such as viscosity fluctuations with time, syneresis, or the process of gelation itself.

The net structure hypothesis meets with a number of objections. Not least in importance is the failure of its proponents to account for the existence of such a structure. In the sol form, they say, the structure does not exist; in the gel form it does exist. What has brought about the change and why was it produced? The sudden appearance of structure must be accounted for.

Again, it is affirmed by this theory that the jelly consists of a sponge-like or honey-comb structure consisting of gelatin as a continuous solid or semi-solid phase, and water (containing inorganic ions and some gelatin molecules in solution) as the dispersed phase. If this were true it should not be difficult to extract the water by moderate pressures, but this cannot be done. Reinke<sup>22</sup> has pointed out that at a pressure of 41 atmospheres the gel of *Laminaria* increases in volume by the absorption of water 16%, and at 1 atmosphere 330%. Posnjak<sup>23</sup> has shown that at 377 cm. of mercury gelatin gel increases in volume nearly 100%, while at 38 cm. the increase is over 250%. Quincke<sup>24</sup> and Hatschek<sup>25</sup> have shown that a volume contraction accompanies the swelling of gelatin to the extent of nearly 2%, and Widemann and Ludeking<sup>26</sup> have reported that 5.7 gram calories of heat were liberated by the swelling of 1 g. of gelatin. These facts are not explained by the assumption that gelatin swells, like a sponge, by the imbibition of water into the porous structure of the gel.

It should also be urged that diffusion and conductivity take place primarily through the continuous phase and not the dispersed phase of a gel, and if the development of the structure in the gel necessitates the assumption of a reversal of phase, as assumed by Fischer<sup>14</sup> and others, it is difficult to understand the nearly identical degrees of diffusion and of conductivity exhibited by the sol and the gel forms, as pointed out by Graham<sup>27</sup> and by Arrhenius,<sup>28</sup> respectively.

In 1920 the writer<sup>29</sup> outlined his views upon the structure of gelatin-water systems. There has since that time been so much work of a more or less confirmatory character that it seems desirable to restate the theory and to add thereto further postulations based upon recent work.

Gelatin sols appear to consist of slightly hydrated molecules united into short threads<sup>30</sup> resembling streptococci. These threads are probably very short, but should be capable of exhibiting mechanical elasticity roughly

<sup>22</sup> Referred to by Hatschek, "Introduction to the Physics and Chemistry of Colloids," J. and A. Churchill, London, 1913, p. 56.

<sup>23</sup> Posnjak, *Kolloidchem. Beihefte*, 3, 417 (1912).

<sup>24</sup> Quincke, *Arch. ges. Physiol.* (Pflüger's), 3, 332 (1870).

<sup>25</sup> Ref. 22, p. 55.

<sup>26</sup> Widemann and Ludeking, *Ann. Physik*, N. F., 25, 145 (1885).

<sup>27</sup> Graham, *Phil. Trans. Roy. Soc.*, 1864.

<sup>28</sup> S. Arrhenius. See Ref. 44.

<sup>29</sup> Bogue, *Chem. Met. Eng.*, 23, 61 (1920).

<sup>30</sup> J. Loeb has found that the assumption of a few united molecules accounts for the differences in the osmotic pressures of calcium and sodium gelatinates. [*J. Gen. Physiol.*, 1, 496 (1919).]

proportional to their length. Procter<sup>31</sup> thinks that at 70°, the solution probably becomes nearly molecular.

A lengthening of these threads seems to take place as the temperature falls, and at the same time the water-absorbing power of the gelatin increases.<sup>32</sup> This accounts for the rapid increase in viscosity with drop in temperature. At temperatures above 40° the change in length of thread or water absorption, per unit change in temperature, is small, but at 30°–20° the change is very great. A solid jelly will result only when the relative volume occupied by the swollen molecular threads has become so great that freedom of motion is lost, and the adjacent heavily swollen aggregates cohere. The rigidity seems to depend on the relative amount of free solvent in the interstices of these aggregates, and on the amount of solvent that has been taken up by the gelatin in a hydrated or imbibed condition. The resiliency or elasticity is probably dependent upon the length and number of the catenary threads. A solution, or change from the gel to the sol form, may result only through the reversal of these processes; that is, a release of a part of the water retained by the heavily swollen molecules, and a partial disintegration of the long enmeshed fibrils of the gel. Any tendency on the part of the fibrils towards an orientation would imply an attractive force between them which would result in a shrinkage. This becomes manifest in syneresis. That some such orienting force does exist is indicated by the lenticular form of bubbles that are generated within gels. The degree of swelling that may be produced in cold water or electrolyte solutions is determined by osmotic forces, as described by Procter, and may be controlled by observing the principal of the Donnan equilibrium as shown by Procter and by Loeb.

The writer<sup>33</sup> has shown that the gel consistency is proportional to the undegraded protein present in a gelatin or glue. It follows, therefore, that the unhydrolyzed gelatin possesses a much greater water-absorbing capacity than the proteoses or peptones. It was also pointed out that the viscosity varied apparently with the size of the colloid aggregate in the solution. The present theory demands that viscosity vary with the degree of water absorption (measured by the rigidity of the gel) and with the size (length) and number of the colloid fibrils (measured by the elasticity of the gel<sup>34</sup>), and also, of course, with the concentration of the solute. The "melting point" was shown<sup>35</sup> to be determined by the protein content and was found to give a "grading" lying between that resulting from measurements of gel strength, and of viscosity at high temperatures (60°). Since it has been indicated in a previous paper<sup>36</sup> that "melting point" is in reality

<sup>31</sup> Procter, Ref. 7, p. 41.

<sup>32</sup> Whether or not this is real hydration is undetermined. McBain and Salmon [*J. Chem. Soc.*, 119, 1374 (1921)] have reported an increase in hydration of soap upon a lowering of the temperature. Jones [*Z. physik. Chem.*, 74, 325 (1910)] has shown that the hydration of molecules and ions increases with a fall in temperature.

<sup>33</sup> Ref. 29, p. 105.

<sup>34</sup> See apparatus of Sheppard, *J. Ind. Eng. Chem.*, 12, 1007 (1920).

<sup>35</sup> Ref. 29, p. 64.

<sup>36</sup> Bogue, *THIS JOURNAL*, 44, 1313 (1922).

only a transitional period between the sol and gel forms, and in this paper that the transition involves only a change in the water-absorbing capacity and the length and number of the colloid molecule-threads, it follows if the above is true that any measure of "melting point" will indicate a resultant between the effects of hydration or water absorption and of length or number of threads, or, differently expressed, a resultant between gel strength and viscosity at high temperatures, which is exactly in conformity with the data reported in an early paper.

Fischer<sup>37</sup> is of the opinion that "the phenomena of hydration (swelling) and of 'solution' while frequently associated are essentially different. Hydration is to be regarded as a change through which the protein enters into physico-chemical combination with its solvent (water); 'solution,' as an increase in the degree of dispersion of the colloid." This is in satisfactory agreement with the ideas expressed above, for although we do not consider that a true solution may exist at low temperatures on account of the heavy hydration or water absorption, yet the change in a jelly upon conversion to a liquid seems to involve a disintegration of the colloid aggregates (increase in degree of dispersion) as well as a lessening in the degree of hydration or water absorption.

The recent work of McBain and his collaborators<sup>38</sup> on the structure of the sol, gel, and curd of soaps is of especial interest, and is in agreement with the theory outlined. They report that in soaps "the colloidal particles in the sol and gel are the same, but whereas in the former they are independent, in a fully formed gel they stick together probably to form a filamentous structure." They further add that "the sol and gel differ only through the mechanical rigidity and elasticity of the gel form." That is precisely what would follow in gelatin sol and gel from the postulations made above, and is a further indication of the gradual nature of the changes which obtain in the sol-gel equilibrium as urged in the previous paper. They state as their belief that a filamentous structure is the general characteristic of soap gels as distinguished from sols. They regard these filaments, however, as normally amicroscopic in size, while in the curds a probably crystalline formation is produced. In gelatin systems the curd or crystalline condition is not known. Harrison<sup>39</sup> reports that he has obtained ultramicroscopic photographs of gelatin and cellulose gels which showed them to consist apparently of "minute portions joined together in a somewhat irregular manner."

Barratt<sup>40</sup> has accepted the fibrillar structure theory as representing most adequately the properties of elastic gels, and reports that ultramicroscopic examination, when it reveals any structure at all, shows the gel to consist "not of liquid droplets enclosed by (solid) septa, as the honeycomb theory requires, but of a mass of intersecting fibrils, which run perfectly straight, and are united at their points of intersection." He concludes that "the real structure of these gels is a fibrillary network, at first amicroscopic and later becoming ultramicroscopic."

A gradual and regular change in properties accompanying the transformation of the sol to the gel or the gel to the sol also supports the theory of structure that has been set forth. This gradual and regular change is indicated by the viscosity-plasticity studies described in a preceding paper;<sup>41</sup> by the finding of Walpole<sup>41</sup> that the refractive index of a gelatin-water system is a linear function of the concentration, and when plotted against the temperature no break occurs in the region of gelation; by the conclusion

<sup>37</sup> Fischer and Coffman, *THIS JOURNAL*, 40, 304 (1918). Fischer, "Soaps and Proteins," John Wiley and Sons, New York, 1921, p. 219.

<sup>38</sup> Laing and McBain, *J. Chem. Soc.*, 117, 1506 (1920). Drake, McBain and Salmon, *Proc. Roy. Soc. London*, 98A, 395 (1921).

<sup>39</sup> Harrison, *Ref. 7*, p. 57.

<sup>40</sup> Barratt, *Biochem. J.*, 14, 189 (1920). *Ref. 7*, p. 49.

<sup>41</sup> Walpole, *Kolloid-Z.*, 13, 241 (1913).

of McBain<sup>43</sup> that the sol and gel forms of soap differ only in the formation of a filamentous structure which accounts for the different properties of the latter; by the reports of C. R. Smith<sup>44</sup> that mutarotation exists between the temperatures 15° and 32°; by the demonstration of Arrhenius<sup>45</sup> that the conductivity of salt:gelatin:water systems was the same in the sol and the gel conditions; and by the findings of Thomas Graham<sup>27</sup> that the rate of diffusion in dilute gels was approximately the same as in pure aqueous solutions.

It is also of interest to note that dibenzoyl-L-cystine which has recently been described by Gortner,<sup>46</sup> and which is capable of forming an elastic gel at concentrations as low as 0.2%, was also shown by an ultramicroscopic examination to have, in the gel condition, a fibrillar structure.

### Specific Influence of Electrolytes

The specific effects of electrolytes upon the sol and gel forms of gelatin were studied in a special series of experiments. The influence of hydrogen-

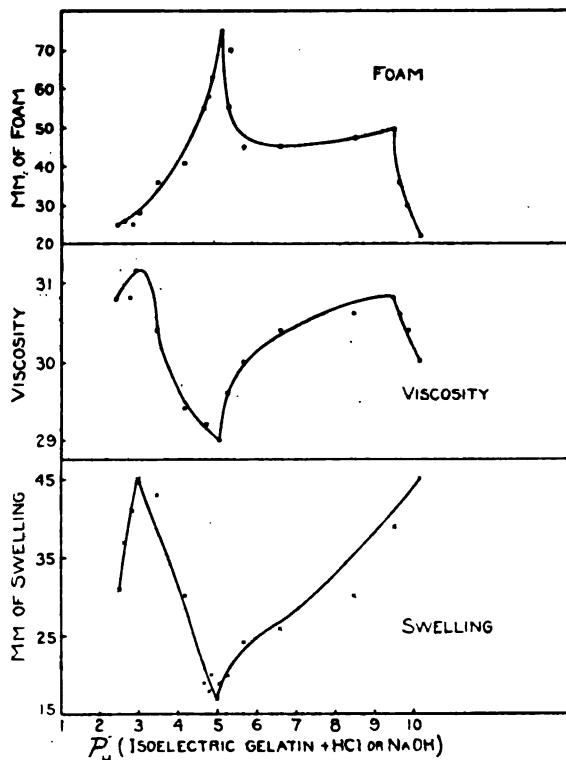


Fig. 1.—Influence of hydrogen-ion concentration on the swelling, viscosity and foam of gelatin.

<sup>43</sup> Laing and McBain, Ref. 38.

<sup>44</sup> Smith, *THIS JOURNAL*, **41**, 146 (1919); Ref. 53.

<sup>45</sup> S. Arrhenius, *Ofvers. Stockh. Akad.*, **1885**, No. 6, p. 121.

<sup>46</sup> Gortner, *THIS JOURNAL*, **43**, 2199 (1921).

ion concentration on the swelling, viscosity, jelly consistency, foam, turbidity and alcohol number was investigated.

The technique of the procedure was adopted from the method reported by Loeb,<sup>46</sup> and is described in detail elsewhere.<sup>46</sup>

An example of the data of these experiments is shown graphically in Figs. 1 and 2.

It will be observed that on the acid side the maximum viscosity and swelling occur at a Sørensen value ( $P_H$ ) of 3.0–3.5, while the maximum jelly consistency is at a  $P_H$  of 4.0–4.5. All of the properties except turbidity and foam appear to have their minimum values, and these two properties their maximum values, at or near the iso-electric point,  $P_H$

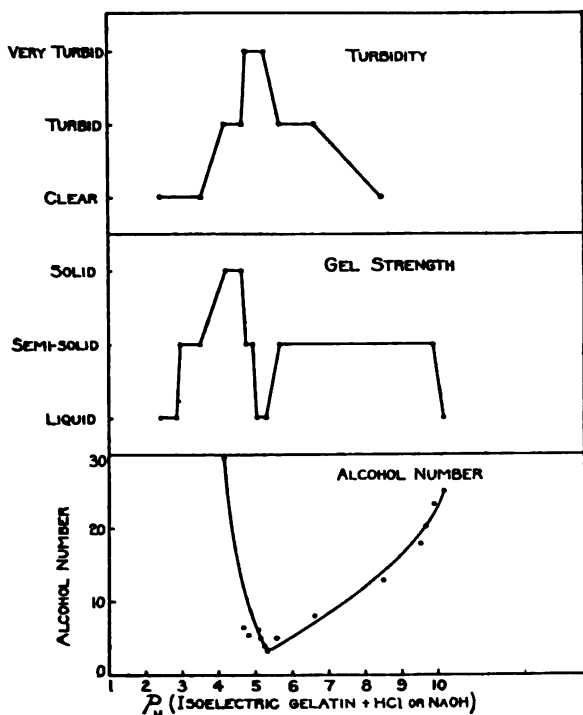


Fig. 2.—Influence of hydrogen-ion concentration on the alcohol number, gel strength and turbidity of gelatin.

4.7–5.0. If acid is present in excess of the optimum specified, the properties again decline. On the alkaline side the properties rise with increasing alkali concentration, but only at very high values of hydrogen-ion concentration do they approach those reached on the acid side.<sup>47</sup>

<sup>46</sup> See Bogue, "The Chemistry and Technology of Gelatin and Glue," McGraw-Hill Co., New York, 1922.

<sup>47</sup> Bogue, *J. Ind. Eng. Chem.*, 14, 32 (1922); see experiments on the alkaline side.

These results are in very good agreement with those published by Loeb.<sup>48</sup>

Similar experiments were performed with sulfuric, phosphoric and lactic acids, with the intent of noting whether all acid ions behaved similarly, or in what respects they differed. The data are given in Fig. 3. They show that phosphoric and lactic acids behave quite similarly to hydrochloric acid, while the swelling and viscosity of the gelatin is much lower in the case of sulfuric acid.

The most probable significance of such behavior has been shown by Loeb, from a study of the relations between the osmotic pressure and con-

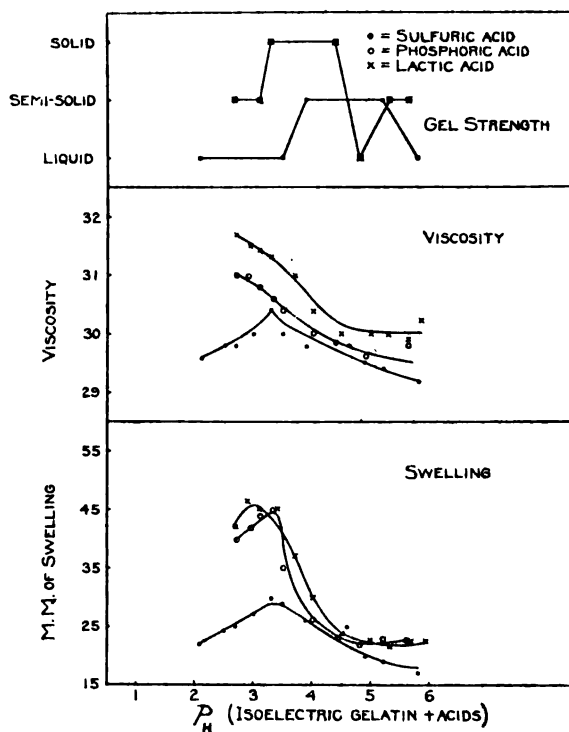


Fig. 3.—Effect of sulfuric, phosphoric and lactic acids on the gel strength, viscosity and swelling of gelatin.

ductivity of such solutions, to lie in a difference in the electrical charge upon the ions in question. All monobasic acids react with gelatin resulting in the formation of a gelatin salt in which the gelatin is positively charged, and all mono-acid bases react with gelatin resulting in the formation of a metal gelatinates in which the gelatin ion is negatively charged.

Lactic acid is monobasic and reacts like hydrochloric. Phosphoric acid is tribasic, but the secondary and tertiary valence force is so slight that with

<sup>48</sup> Loeb, *J. Gen. Physiol.*, 1, 39, 237, 363, 483, 559 (1918-19).

gelatin the acid acts only as monobasic, so on treating it as such and using molecular equivalent quantities it acts as does hydrochloric. Sulfuric acid is dibasic, and Loeb has shown that both valences function in reactions with gelatin.<sup>49</sup> The swelling, viscosity, etc., of gelatin sulfate are consequently much lower than those of the corresponding salt of a monobasic acid. Furthermore, on the acid side of the iso-electric point gelatin can combine only with anions and is uninfluenced by cations, while on the alkaline side of that point the gelatin can combine only with cations and is uninfluenced by anions.

A further very exact study was made of the effect of hydrogen-ion concentration upon viscosity, using gelatin of 3 typical kinds: iso-electric gelatin, normal gelatin which was calcium gelatinates of  $P_H$  5.8, and gelatin chloride of  $P_H$  3.5. The results of these experiments have been described in a previous report.<sup>50</sup> They show the same behavior as the experiments above described, but at varying concentrations of gelatin.

**Discussion of Results.**—The foregoing data are found to furnish additional evidence in favor of the theory that has been described. The swelling may be taken as a measure of the water absorption or hydration and this is found to be parallel to the viscosity. An increase in viscosity must be due to an increase in the effective volume of the gelatin in the solution. This volume is obviously at a minimum at the iso-electric point which signifies that hydration is least at that particular hydrogen-ion concentration. This may be due to the fact that at that hydrogen-ion concentration gelatin is un-ionized and ions appear to be capable of greater hydration than un-ionized molecules.<sup>51</sup> The viscosity of iso-electric gelatin increases upon standing, however, at a greater rate than at any other hydrogen-ion concentration, and this appears to be due to the very marked insolubility of the gelatin at that point, for the tendency of the gelatin molecules and colloid fibrils to increase in size by flocculation or polymerization is so decided at the iso-electric point that it is easily observable under the ultramicroscope. It is especially significant to observe that the jelly consistency of iso-electric gelatin (see curves) becomes very low at that point which also indicates a low degree of hydration.

The increases in viscosity observed by raising or lowering the hydrogen-ion concentration from the iso-electric point are apparently attributable to a variation in the degree of hydration or water absorption, as shown by the parallelism of the viscosity and swelling curves. The sudden

<sup>49</sup> The primary ionization of phosphoric acid is about fifty thousand times the secondary ionization, and this in turn about five hundred thousand times the tertiary ionization. In the case of sulfuric acid, however, the primary ionization is only about 33 times the secondary ionization. (See Stieglitz, "Qualitative Chemical Analysis," The Century Co., New York, I, p. 104.)

<sup>50</sup> Bogue, *THIS JOURNAL*, 43, 1764 (1921).

<sup>51</sup> Jones, *Am. Chem. J.*, 34, 291 (1905).



drop in both viscosity and swelling at a Sørensen value above 9 or below 3 seems to be due to a "solution" or breaking down of the colloid molecule-threads, and this disintegration is accompanied by a corresponding lessening in the ability of the smaller aggregates or molecules to take up water in hydrated or imbibed form. That this reasoning is justified is further evidenced by the known inability of the proteoses and peptones to become swollen to anything like the degree attained by the gelatin aggregate.

The depressing influence of inorganic ions on the swelling and viscosity of the gelatin is probably partly attributable to the withdrawal of water from the hydrated gelatin by these ions. And since the high viscosities are due to the heavily swollen gelatin aggregates, any decrease in the degree of such hydration or imbibition must be reflected by a drop in the viscosity of the solution. Divalent ions appear to be capable of greater hydration than monovalent ions and should therefore be expected to be capable of withdrawing larger amounts of water from the gelatin particles. From the studies of Fischer<sup>52</sup> it is also shown that divalent base soaps and proteinates dissolve less water than monovalent ones.

The turbidity curves indicate that the greatest opacity results from the largest aggregates of least swollen particles. This maximum of opacity occurs at the iso-electric point. Any decrease in the size of the aggregates or increase in the water absorption results in greater clarity or transparency of the solution.

The foaming qualities appear to be influenced in a manner similar to the turbidity, the maximum of foam being obtained at the iso-electric point. This is exactly what would be expected for, since the foam consists of bubbles of air retained by a continuous film, only molecules that have a strong tendency to adhere to each other would be efficacious in film formation. At the iso-electric point gelatin molecules show their maximum tendency to form large aggregates.

The alcohol number is at its minimum value near the iso-electric point, and rises rapidly to infinity on the acid side and somewhat less rapidly on the alkaline side. Since the alcohol number refers to the precipitability of gelatin by alcohol it would be expected that the larger the molecular aggregate, and the less the water content of the aggregate, the more readily would such precipitation be brought about. This is especially significant in that alcoholic precipitation of proteins probably consists essentially of a dehydration or extraction of water. Therefore, in systems that are only slightly hydrated, precipitation is readily brought about by alcohol, but in systems containing large amounts of absorbed water the dehydrating influence of added alcohol may be insufficient to effect precipitation.

<sup>52</sup> Ref. 14, p. 14.

### Mutarotation

In order to test the theory further the data of C. R. Smith<sup>53</sup> on mutarotation were examined critically in their applications to the sol-gel equilibrium. The change in specific rotation, or mutarotation, of gelatin solutions of a constant concentration upon reduction of the temperature from 35° to 15° was found to drop off very markedly with a decreasing jelly consistency of the gelatin or glue employed. That is, the mutarotation was highest in a (3%) solution of a gelatin which was capable of gelling (at 15°) at a concentration of about 0.56% and very low in a (3%) solution of gelatin which would gel (at 15°) only when the concentration had been raised to 2.00% or higher. To have a more concise picture of the exact relations the data of Smith have been plotted, the ordinate representing the mutarotation (15–35°) and the abscissa the minimum amount of gelatin required to produce a standard jelly at 15°. This curve is shown in Fig. 4.

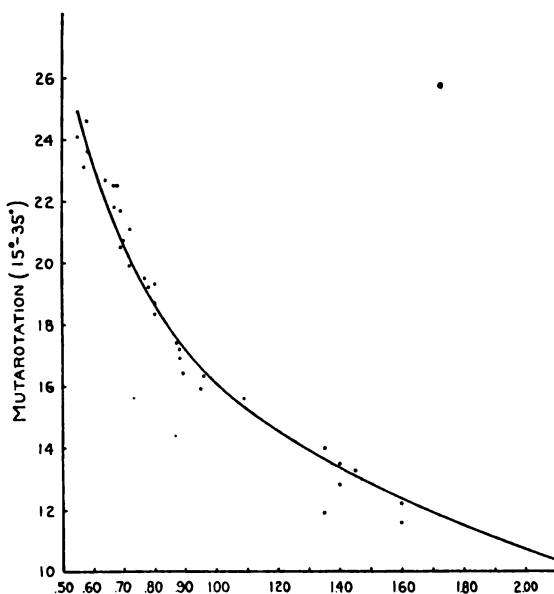


Fig. 4.—Mutarotation and jellying power.

There are many minor discrepancies observable, but these are attributable to the failure of the method employed for measuring jelly consistency<sup>54</sup> to distinguish between rigidity and elasticity of the gel. The general tendency of the curve is, however, incontrovertible.

<sup>53</sup> Smith, *J. Ind. Eng. Chem.*, 12, 878 (1920).

<sup>54</sup> A standard viscosity which would permit a bubble of air to rise through a tube of the gelatin sol-gel at an arbitrarily selected rate.

Since the jellifying power of a gelatin solution has been shown<sup>22</sup> to be proportional to the content of unhydrolyzed protein present, it follows that the mutarotation is also proportional to the protein content. We have given evidence which indicates that the proteins (of gelatin) are capable of vastly greater hydration than the proteoses and peptones. It appears, therefore, necessary to conclude that the mutarotation, or increase in specific rotation upon reduction in temperature ( $35^{\circ}$  to  $15^{\circ}$ ) must be dependent for its existence upon the greatly increased water absorption and aggregation or polymerization which such unhydrolyzed proteins are found to undergo upon similar reductions in temperature.

### The Occlusion Theory

Loeb<sup>18</sup> has recently questioned the whole conception of hydration, in the sense in which the term was used by Pauli, at least in so far as it applies to solutions of the proteins (gelatin, casein and crystalline egg albumin), and finds it impossible to reconcile the results of his experiments upon the viscosity and osmotic pressure of such solutions with the early hydration theory.

To study the question Loeb performed a long series of experiments with solutions and suspensions of gelatin. He found that the influence of electrolytes on the viscosity of *suspensions* of powdered particles of gelatin in water was similar to their influence on the viscosity of *solutions* of the gelatin in water. He found it unnecessary to assume that the high viscosity of proteins is due to the existence of a different type of viscosity from that existing in crystalloids, but that such high viscosities could be accounted for quantitatively and mathematically on the assumption that the *relative volume* of the gelatin in the solution is comparatively high. And since iso-electric gelatin is not appreciably ionized, the large volume cannot be due to an hydration of gelatin *ions*. Loeb therefore postulates that the high volume of gelatin solutions is caused by the existence in the gelatin solution of "submicroscopic pieces of solid gelatin occluding water, the relative quantity of which is regulated by the Donnan equilibrium." This view was supported by experiments on solutions and suspensions of casein chloride and gelatin chloride in which it was shown that viscosity was due chiefly to the swelling of solid particles, occluding quantities of water regulated by the Donnan equilibrium, and that the breaking up of these solid particles into smaller particles, no longer capable of swelling, diminished the viscosity.

Loeb asks why such substances as amino acids and crystalline egg albumin behave so differently from gelatin. But such substances should not be expected to show variations in degree of hydration with changes in hydrogen-ion concentration of a nature parallel to those resulting from similar changes in gelatin solutions. The writer<sup>23</sup> has already shown

many differences in fundamental properties between true gelatin, proteose and peptone. Thus the swelling, viscosity, and power of gelation vary directly as the gelatin content (of a commercial gelatin or glue), and probably as the size of the gelatin aggregate, and further evidence has been given<sup>47,60</sup> that these variables are controlled to a large extent by the degree of hydration or imbibition.

To understand the importance which Loeb attaches to his whole argument against the hydration theory, it is necessary to emphasize that the term *hydration* was used in a very specific sense. By it Loeb referred exclusively to the hydration conception postulated by Kohlrausch and extended by Pauli.<sup>65</sup> According to this conception each individual protein ion is surrounded by an enormous shell of water molecules, while the non-ionized molecule of protein has no, or little, such a shell. If this theory were correct, the variations in swelling, viscosity, osmotic pressure, etc., should follow the variations in degree of ionization of the protein; but Loeb has shown by conductivity measurements that this is not the case.

The sense in which the term *hydration* has been used in the present report is that adopted by Wo. Ostwald and Martin Fischer to signify only the taking up of water by the protein ions, molecules, or particles, and without any necessary implication upon the mechanism of such combination. Loeb has confined his argument for the most part to a consideration of the intermolecular mechanism by which such combinations with water may be most satisfactorily accounted for. The two points of view seem to be in no way contradictory.

### Summary

The several theories of gel structure have been reviewed and discussed, and the postulations of the writer that were made in 1920 are repeated and amplified. Many contemporary investigations have been found to support a catenary or fibrillar structure hypothesis, and are set forth.

The premises of this theory are as follows. The sol consists of slightly hydrated or swollen molecules united into short chains. When the temperature falls the threads increase in length and number, and their power of water absorption increases, resulting in an increase in viscosity. A solid jelly results when the relative volume occupied by the swollen molecular threads has become so great that freedom of motion is lost, and the adjacent heavily swollen aggregates cohere. The rigidity is dependent upon the relative amount of free solvent in the interstices of the aggregates, and on the amount of solvent that has been taken up by the gelatin in a hydrated or imbibed condition. The resiliency or elasticity is dependent upon the length and number of the catenary threads.

<sup>65</sup> Personal communication from Jacques Loeb.

Solution is the reverse of gelation. Swelling is determined by osmotic forces and the Donnan equilibrium.

The influence of electrolytes, of varying hydrogen-ion concentration, and of the valence of the combining ion has been studied upon several of the characteristic properties of gelatin and found to be entirely in agreement and to give additional evidence in support of the theory presented.

Data on the mutarotation of gelatin were found to be in accord with the theory.

The occlusion theory of Loeb is reviewed and found not to be out of harmony with the present theory, but rather to explain the distribution of absorbed water and its variation with hydrogen-ion concentration mathematically in terms of the Donnan equilibrium.

PITTSBURGH, PENNSYLVANIA

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]  
**THE REACTIONS OF THE ARSINES. II. CONDENSATION  
OF AROMATIC PRIMARY ARSINES WITH ALDEHYDES<sup>1</sup>**

BY CHARLES SHATTUCK PALMER WITH ROGER ADAMS<sup>2</sup>

Received March 23, 1922

The arsines, in spite of their close relationship in constitution to the amines, have been investigated only to a slight extent. The known reactions of the primary arsines are limited to: (1) the ready oxidation by air or inorganic oxidizing agents to arseno compounds, arsine oxides or arsonic acids;<sup>3</sup> (2) the replacement of hydrogen bound to arsenic by halogens or sulfur by treatment with halogens, sulfur, or compounds which readily give up these elements;<sup>4</sup> (3) the formation of quaternary arsonium halides by heating with alkyl halides;<sup>5</sup> (4) the condensation with compounds of the type  $RAsO$ ,  $RSbO$ ,  $RAsCl_2$ ,  $RSbCl_2$ ,  $SbCl_3$ ,  $BiBr_3$ , etc., to yield compounds of the type  $RAs=AsR$ ,  $RAs=SbR$ ,  $RAs=BiBr$ , etc.<sup>6</sup> In addition might be mentioned the fact that the arsines

<sup>1</sup> The expenses involved in the research described in this communication were partially defrayed by funds granted by the United States Interdepartmental Social Hygiene Board.

<sup>2</sup> This communication is an abstract of a thesis submitted by Charles Shattuck Palmer in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Chemistry at the University of Illinois. It also includes a description of a portion of the work offered by the following men in fulfillment of the requirements for the degree of Master of Science in Chemistry: W. A. Carothers, E. E. Parks, G. O. Burr, J. S. Pierce.

<sup>3</sup> *Ber.*, 34, 3597, 3599 (1901); *Am. Chem. J.*, 33, 124, 144, 149 (1905); 40, 105ff (1908).

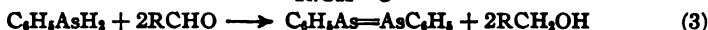
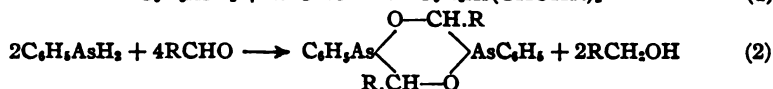
<sup>4</sup> *Am. Chem. J.*, 33, 126, 150 (1905); 40, 105 (1908).

<sup>5</sup> *Ibid.*, 33, 128, 145, 152 (1905); 40, 112 (1908).

<sup>6</sup> *Ibid.*, 40, 108 (1908); *Ber.*, 46, 3564 (1913). Ger. pat. 254,187; 269,743; 269,744; 269,745; 270,259.

show practically no basicity. The lack of study of the more common reactions such as take place with primary amines has led to a further investigation of the arsines. This paper reports the results of the condensation between primary aromatic arsines and aldehydes.

In the literature may be found two instances in which attempts have been made to condense arsines with aldehydes. The first is a statement by Dehn<sup>7</sup> that formaldehyde and gaseous methylarsine do not react. It is also stated in a German patent<sup>8</sup> that 3-amino-4-hydroxyphenylarsine reacts with benzaldehyde-*m*-sulfonic acid, but in this instance only the amino group reacts with the aldehyde. In a preliminary article published a short time ago,<sup>9</sup> it was pointed out that phenylarsine reacts readily with aldehydes to give an addition compound composed of two molecules of aldehyde and one of arsine. Further investigation of this reaction has shown that the conditions are a very important factor in the nature of the products obtained. It is possible to cause the aromatic arsines to react with the aldehydes in three ways as illustrated by Equations 1, 2 and 3.



The first reaction takes place readily to give yields of 60–95% when phenylarsine and an excess of aromatic or aliphatic aldehyde and a little conc. hydrochloric acid, with or without a solvent, are stirred together vigorously and the temperature kept down by means of ice water. For the condensation with aromatic aldehydes, the best results are obtained by the use of anhydrous hydrogen chloride but this method cannot be employed with the aliphatic aldehydes. These products,  $\text{C}_6\text{H}_5\text{As}(\text{CHOHR})_2$ , are, in general, oils in the aliphatic series and solids in the aromatic series, and possess decided stability toward water, dil. alkalis, cold or hot, and cold dil. acids. This behavior forms a striking contrast to that of the isomeric esters<sup>10</sup> of phenylarsenious acid,  $\text{C}_6\text{H}_5\text{As}(\text{OCH}_2\text{R})_2$ .

The substances derived from aliphatic aldehydes and from some of the aromatic aldehydes are oxidized slowly in air with the formation of an arsonic acid and aldehyde. The oxidation goes much more rapidly when the substances are dissolved in a solvent such as carbon tetrachloride, even causing the reaction mixture to heat up under these conditions.



Oxidizing agents such as potassium permanganate and nitric acid cause

<sup>7</sup> Dehn, *Am. Chem. J.*, **40**, 108 (1908).

<sup>8</sup> Ger. pat. 272,035.

<sup>9</sup> *THIS JOURNAL*, **42**, 2375 (1920).

<sup>10</sup> *Ann.*, **320**, 286 (1902).

the decomposition of both the aliphatic and aromatic aldehyde derivatives to take place in the same way as the oxidation with air. It is particularly noticeable that these substances with oxidizing agents, halogens, phosphorus pentachloride, and phenylarsenious chloride, act exactly as though they were mixtures of phenylarsine and aldehyde. These reactions are described in more detail in the experimental part of this communication.

The aliphatic derivatives may be titrated quantitatively in ether solution with iodine, under which conditions the following reaction immediately takes place.



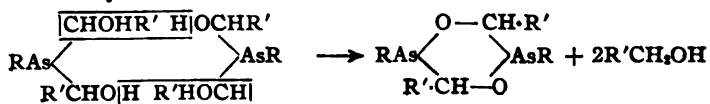
The aromatic aldehyde derivatives react slowly with iodine solution but quantitative titration is impossible.

The compounds are decidedly stable toward reducing agents and also toward dehydrating agents (with the exception of anhydrous hydrochloric acid, acid chlorides or acid anhydrides under certain conditions).

The aliphatic aldehyde compounds form unstable addition products with halogen acids; no such addition products with other tertiary arsines have been described. The substances also form characteristic stable addition compounds with chloroplatinic acid.

It might be expected that the products would show reactivity with acid chlorides or anhydrides or with other hydroxyl group reagents. They do not, however, give the desired derivatives. Moreover, they do not react with methyl or ethyl magnesium iodide to give methane or ethane. The action of the acid chlorides and anhydrides is explained below but the unexpected non-reactivity of the Grignard reagent is not yet clearly understood. It seems probable that a soluble addition compound is immediately produced which prevents a reaction with the hydroxyl groups. Water decomposes the Grignard mixture into the unchanged aldehyde-arsine addition product and the normal decomposition products of the Grignard reagent. In spite of the fact that no simple derivatives of these aldehyde-arsine compounds could be obtained except the addition products with chloroplatinic acid, the formula which has already been suggested is the only one which will account for the known reactions.

The cause for the non-formation of the normal derivatives of the hydroxyl groups can be accounted for by the fact that certain dehydrating agents such as acetyl chloride, acetic anhydride or even anhydrous hydrogen chloride cause a secondary reaction to take place readily. Two molecules of these *bis-α*-hydroxy tertiary arsines by this treatment lose 2 molecules of alcohol with the production of rings which may be designated as tetrahydro-1,4,2,5-dioxdiarsines.



These compounds are thus derivatives of the basic ring 1,4,2,5,-dioxdiar-

sine having the structure . They represent the second

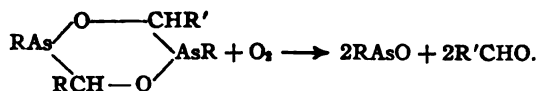
type of substance which can be obtained directly from primary aromatic arsines and aldehydes. They are formed by merely allowing a mixture of aromatic arsine and aldehyde to remain for a day or two in the presence of anhydrous hydrogen chloride at ordinary temperature. Under these conditions, the amount of the product which consists of *bis*- $\alpha$ -hydroxy tertiary arsine is small and the amount of the tetrahydro-dioxdiarsine large.

The formation of the tetrahydro-dioxdiarsines as just described undoubtedly takes place in two steps—the formation first of the *bis*- $\alpha$ -hydroxy tertiary arsines and then the further condensation of these latter products to tetrahydro-dioxdiarsines. This mechanism was proved by treating pure *bis*- $\alpha$ -hydroxy tertiary arsines with dry hydrogen chloride and obtaining from the reaction mixture, after standing several days, tetrahydro-dioxdiarsines. The presence of the water in the hydrochloric acid used to catalyze the formation of the *bis*-( $\alpha$ -hydroxyalkyl) arsines evidently prevents further condensation. No ring compounds have been isolated as yet when using aromatic aldehydes; as mentioned before, anhydrous hydrochloric acid causes aromatic aldehydes and arsines to condense to a very good yield of *bis*-( $\alpha$ -hydroxybenzyl) arsines and no secondary condensation apparently takes place.

A reaction of particular interest is that between paraformaldehyde and phenylarsine in the presence of aqueous hydrochloric acid. The condensation is carried out in the usual way but a product having the formula  $C_6H_5As(CH_2OH)_2$  cannot be isolated. During the distillation decomposition occurs, and the final product is the corresponding tetrahydro-dioxdiarsine.

These ring compounds are unaffected by long standing with water, dil. acids or alkalis, or even hot 10% alcoholic potassium hydroxide solution.

The tetrahydro-dioxdiarsines oxidize in the air and form arsine oxides and aldehyde according to the following equation.



The stability of the formaldehyde derivative is much less than that of the acetaldehyde compound or higher homologs. With oxidizing agents such as nitric acid, phenylarsonic acid and aldehyde, or phenylarsonic acid and aldehyde oxidation products are formed.

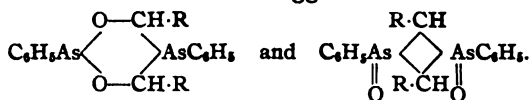


With iodine in ether solution, the substances decompose to aldehyde and arsine di-iodide; the compounds, however, cannot be titrated quantitatively with iodine solution.

The substances form double salts with chloroplatinic acid, and cupric chloride, both of which are stable to air although the latter have a tendency to turn green on standing. They do not form the unstable halogen acid addition products noticed with the *bis*-( $\alpha$ -hydroxyalkyl) arsines.

With phosphorus pentachloride there are formed aldehyde and phenyl dichloro-arsine.

The structure of the tetrahydro-dioxdiarsines can be determined definitely from the mode of formation. The alcohol, which is produced at the same time, may be isolated as such, or in the form of an acetal or, ester; moreover the molecular weight and analysis indicate the formula given. Two other possible structures which suggest themselves are



The first of these two cannot be correct since all arsenic compounds of the general formula  $\text{RAs}(\text{OCH}_2\text{R})_2$ , into which class this compound falls, are decidedly unstable to water and aqueous alkalis; the tetrahydro-dioxdiarsines are stable to water and alkali. The second structure will not explain the decomposition of the products into phenyl-di-iodo-arsine and aldehyde by the action of iodine; it is also inconsistent with the oxidation by air and with the physical properties of the products.

The third equation given at the beginning of this communication illustrating the reducing power of the arsines, takes place when a higher temperature is used with or without a catalyst, or when the arsines and the aldehydes are allowed to stand for a long time at room temperature without a catalyst. Under any of these conditions the formation of the condensation products is completely prevented. Thus it has been found that a mole of benzaldehyde and a mole of phenylarsine, when boiled in the presence of acetic acid as a solvent, yield an almost quantitative amount of arsenobenzene and benzyl acetate. Other aromatic aldehydes give the same results. If, however, aldehydes and arsines are mixed in different proportions from those just mentioned, the reactions take place in a somewhat different way and more complex products are produced. A further study of the reduction products of aldehydes and ketones is now being made.

Chloral, when treated with phenylarsine, yields phenylarsenious chloride, illustrating the ease with which hydrogen in the arsines is replaced by halogen.

The formation of the aldehyde-arsine addition compounds from aldehydes and arsines makes it evident that the carbonyl group in aldehydes

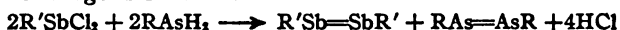
and ketones will not react with the primary arsine group with the elimination of water, such as takes place when an aldehyde or ketone reacts with a primary amine. It seems probable, therefore, that the general reaction which has been studied by other investigators, whereby the primary arsines condense with compounds of the type  $\text{RASO}$  and  $\text{RSbO}$  to give  $\text{RAs=AsR}$  and  $\text{RAs=SbR}$ , does not take place so simply as is ordinarily explained, namely, by the direct elimination of water. It seems much more likely that the arsine reduces the arsine or stibine oxides to corresponding arseno or stibino compounds and is itself oxidized to another arseno compound.



The rearrangement of two arseno compounds into the unsymmetrical derivative takes place very smoothly and practically quantitatively.<sup>11</sup>

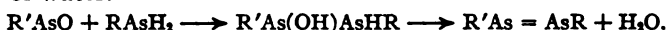


There are thus formed exactly the same products as obtained by the simpler mechanism. It is probable that the reactions between the primary arsines and the arsine halides, bismuth halides or stibine halides, take place in an analogous manner.



It is, of course, possible that in the reaction just mentioned reduction occurs in such a way that nascent radicals having the formulas  $\text{RAs=}$ ,  $\text{RSb=}$ ,  $\text{R}'\text{As=}$  are first formed and that these then combine directly to give the unsymmetrical arseno or the corresponding arsenic antimony compounds rather than to give symmetrical compounds as intermediates.

It is also possible that there is merely an addition product formed first from the oxide and arsine which subsequently decomposes with the elimination of water.



## Experimental

### Phenylarsine and Derivatives

**Phenylarsonic Acid,**<sup>12</sup>  $\text{C}_6\text{H}_5\text{AsO}_3\text{H}_2$ .—For the production of phenylarsonic acid on a large laboratory scale, a 25-liter cylindrical copper tank, provided with mechanical stirrer, is employed. In the tank are placed 4 liters of water, 2 kg. of anhydrous sodium carbonate, 1 kg. of technical arsenious oxide (about 20% excess), and 45 g. of crystallized copper sulfate. All of the solid material does not dissolve unless the solution is heated. The stirrer is started and the walls of the tank are cooled by several streams of water. As soon as the temperature of the arsenite solution falls to 15°, (part of the sodium ar-

<sup>11</sup> Ger. pat. 251,104; Brit. pat. 17,482; *Ber.*, 49, 1648 (1916). Ger. pat. 253,226; 270,255.

<sup>12</sup> *Ber.*, 9, 1568 (1876); 10, 626 (1877); 15, 1954 (1882); 27, 265 (1894); 41, 1855 (1908); 54, 438 (1921). *Ann.*, 201, 203 (1880); 320, 293 (1902). Ger. pat. 250,264; 254,092; 264,924. *J. Ind. Eng. Chem.*, 11, 824 (1919). The method of Schmidt, *Ann.*, 421, 168 (1920), is unsuitable for runs of any considerable size.

senite precipitates at this temperature), the addition of diazo solution is begun. It is found convenient to prepare the latter in four portions. A mixture of 186 g. of aniline, 400 cc. of conc. hydrochloric acid, 1 liter of water and sufficient ice to bring the total volume to 3 liters is made and placed in a 4-liter Florence flask. This mixture is diazotized in the usual manner with a concentrated solution of 140 g. of sodium nitrite. Three hours or more are required for running four of these diazo solutions into the arsenite, the temperature of the latter being maintained at 15°. During this addition, foaming can be controlled by regulating the speed of stirring and also by adding about 10 cc. of benzene whenever excessive foaming threatens to occur.

Stirring is continued for one hour after all the diazo solution has been added. The mixture is now filtered and the filtrate concentrated to a volume of approximately 5 liters; this is deep brown in color. Conc. hydrochloric acid is added in small portions and the tarry material which separates is filtered off. The acid is added until after filtering a clear, pale yellow solution results. The phenylarsonic acid is now precipitated by the addition of more hydrochloric acid. An excess must be avoided since it causes a certain amount of the phenylarsonic acid to go into solution. When this neutralized mixture has cooled, the product is filtered off and washed with a little distilled water. Small quantities of phenylarsonic acid remaining in the filtrate may be precipitated as the ferric salt by adding ferric chloride.<sup>13</sup> The average yield of white or cream colored product exceeds 800 g. (50% of that calculated) and in many cases runs well over 1000 g. This crude material is perfectly satisfactory for use in the preparation of phenylarsine. If, however, a pure product is desired, it may be crystallized from water which frees it from small amounts of sodium chloride. The product is then practically white and softens at 158°, passing into the infusible anhydride,  $C_6H_5AsO_3$ .

**Phenylarsine,**<sup>14</sup>  $C_6H_5AsH_4$ .—A 5-liter round-bottom flask is provided with a long bulb reflux condenser. A 2-hole stopper at the upper end of the condenser carries a 2-liter dropping funnel and an outlet tube connected to a mercury-filled U-tube. In the flask is placed an intimate mixture of 400 g. of crude phenylarsonic acid made in the way just described, and 800 g. of amalgamated zinc dust, a little water and 1 liter of ether. Two liters of conc. hydrochloric acid is added drop by drop; by proper regulation the apparatus can be allowed to run overnight without attention. When the reduction is complete, the condenser is removed and replaced by a 2-hole stopper carrying a 16cm. funnel and a delivery tube. By pouring water into the funnel, the ether layer is forced through the delivery tube into a 2-liter separatory funnel filled with carbon dioxide. Lumps of anhydrous calcium chloride are added. When dry, the solution is transferred in portions to a 500cc., Claisen distillation flask filled with carbon dioxide, with fractionating column side-arm fitted with a receiver of equal size. Most of the ether is removed by heating on the steam-bath, a constant current of carbon dioxide being passed through the apparatus. The distillation is continued under diminished pressure, the receiver being cooled in ice and water. By a little practice it is found possible to change receivers without oxidation of the phenylarsine, so that use of a Brühl apparatus suggested by a previous investigator is unnecessary. The product boiling at about 93° at 70 mm. is collected. A redistillation is advisable if a very pure product is desired, but the material obtained at this point was used directly for the condensations with aldehydes described in this communication. When the distillation is complete, carbon dioxide is admitted until atmospheric pressure is reached, and the product sealed in large test-tubes which have previously been constricted near the open end and filled with carbon dioxide. The best yield obtained was 83% of the calculated amount, obtained by using recrystallized phenylarsonic acid; the average yield, using crude arsonic acid, was between 50 and

<sup>13</sup> Suggested by Mr. J. L. Hall.

<sup>14</sup> *Ber.*, 34, 3598 (1901). *Am. Chem. J.*, 33, 147 (1905). *Chem. Ztg.*, 1912, 1099.

60% of the calculated amount, depending largely on the grade of crude arsonic acid used. Phenylarsine is a clear, colorless liquid of disagreeable odor. It causes painful blisters when it comes in contact with the skin and is highly irritating to the mucous membrane. Constants not given in the literature are:  $d_{25}^{25}$ , 1.349;  $n_D^{25}$ , 1.6082.

**General Method for the Preparation of Aryl Bis- $\alpha$ -hydroxyalkyl Arsines.**—A 500cc. wide-mouth bottle is provided with a mechanical stirrer. Carbon dioxide is passed into the bottle and then 100 g. (1 mol.) of aryl arsine and a few cubic centimeters of conc. hydrochloric acid are added. The mixture is cooled well in an ice-bath, the stirrer started, and 2 moles of aliphatic aldehyde or polymeric aldehyde are added drop by drop. When using aldehydes of a volatile nature it is advisable to add a slight excess instead of exactly 2 moles. In small runs mechanical stirring is not necessary, merely occasional shaking by hand. The carbon dioxide is passed in continuously and stirring continued for a couple of hours after the addition of the aldehyde. The reaction mixture is then shaken with a little fused potassium carbonate to remove the hydrochloric acid, any arylarsonic acid which is formed, and moisture. The products are distilled under diminished pressure.

If desired, the ether solution formed in the preparation of the aryl arsine may be utilized directly in synthesizing the aldehyde addition compound. In this way a larger yield per gram of arylarsonic acid can be obtained.

The substances which are produced as described above are insoluble in water but readily soluble in organic solvents. They are perfectly stable toward dil. alkalis even on boiling. They are also stable toward dil. acid, but decompose gradually on standing with conc. hydrochloric acid at room temperature, and rather rapidly on heating.

The physical constants described under the individual compounds were taken in every instance on freshly prepared products. If allowed to stand without proper precautions to prevent oxidation, the indices of refraction soon become considerably lower, due undoubtedly to oxidation.

Certain of the substituted arsines were prepared and condensed with aldehydes before it was realized that precautions must be taken with the products to prevent gradual decomposition in the air. For this reason, a few of the substances when analyzed showed a variation from the theoretical percentage compositions.

**Bis-( $\alpha$ -hydroxyethyl)phenylarsine,  $C_6H_5As(CHOHCH_3)_2$ .**—From 100 g. of phenylarsine, 2 cc. of conc. hydrochloric acid and 75 g. of acetaldehyde or paraldehyde, 127 g. (81%) of redistilled product is obtained boiling at 175–176° at 22 mm. The product is a colorless oil;  $d_{25}^{25}$ , 1.252;  $n_D^{25}$ , 1.5619.

**Analyses.** Subs., 0.2637:  $CO_2$ , 0.4743;  $H_2O$ , 0.1420. Subs., 0.1356, 0.1274: 10.2 cc., 9.65 cc. iodine (1 cc. = 0.0041 g. As). Subs., 0.6072: benzene, 22.0: f. p. lowering, 0.564°. Calc. for  $C_{10}H_{14}O_2As$ : C, 49.59; H, 6.19; As, 30.99; mol. wt. 242. Found: C, 49.03; H, 6.02; As, 30.83, 31.05; mol. wt. 246.

**Bis-( $\alpha$ -hydroxy-*n*-propyl)phenylarsine**,  $C_6H_5As(CHOHC_3H_7)_2$ .—From 17 g. of propionic aldehyde and 23 g. of phenylarsine with 1 cc. of hydrochloric acid, 28 g. (70% yield) of product is obtained boiling at 196–197° at 24 mm. The product is a colorless oil;  $d_{25}^{25}$  1.176;  $n_D^{25}$  1.5425.

**Analysis.** Subs., 0.2043: 13.8 cc. iodine (1 cc. = 0.0041 g. As). Calc. for  $C_{12}H_{18}O_2As$ : As, 27.77. Found: 27.69.

**Bis-( $\alpha$ -hydroxy-*n*-butyl)phenylarsine**,  $C_6H_5As(CHOHC_4H_9)_2$ .—From 50 g. of phenylarsine, 50 g. of butyraldehyde and 1 cc. of conc. hydrochloric acid, 75 g. of pure product is obtained. The substance is a colorless oil boiling at 187° at 10 mm.;  $d_{25}^{25}$  1.116;  $n_D^{25}$  1.5271. A mistake was made in the refractive index as reported in the preliminary paper.<sup>15</sup>

**Analyses.** Subs., 0.2296, 0.2210: 14.0 cc., 13.5 cc. iodine (1 cc. = 0.0041 g. As). Calc. for  $C_{14}H_{20}O_2As$ : As, 25.17. Found: 25.00, 25.05.

**Bis-( $\alpha$ -hydroxyisovaleryl)phenylarsine**,  $C_6H_5As[CHOHC_4H_9(iso)]_2$ .—From 16 g. of isovaleraldehyde, 15 g. of phenylarsine and 0.5 cc. of conc. hydrochloric acid, a colorless oil (59% yield) is obtained boiling at 170° at 6 mm.;  $d_{25}^{25}$  1.079;  $n_D^{25}$  1.5202. By cooling it well with ice and salt, the product solidifies. On recrystallization from ether, needles form which melt sharply at 62°.

**Analysis.** Subs., 0.1980: 11.1 cc. iodine (1 cc. = 0.0041 g. As). Calc. for  $C_{16}H_{22}O_4As$ : As, 22.87. Found: 22.98.

**Bis-( $\alpha$ -hydroxy-*n*-heptyl)phenylarsine**,  $C_6H_5As(CHOHC_7H_{15})_2$ .—From 15 g. of oenanthol and 8 g. of phenylarsine with 0.5 cc. of conc. hydrochloric acid, a good yield of substance is produced. It cannot be distilled even under diminished pressure without considerable decomposition. A small amount of distilled material was obtained, b. p. 263–264° at 2 mm.;  $d_{25}^{25}$  1.069;  $n_D^{25}$  1.4650. The substance solidifies, but does not crystallize, in a freezing mixture.

**Analysis.** Subs., 0.1798: 7.8 cc. iodine (1 cc. = 0.00446 g. As). Calc. for  $C_{20}H_{30}O_2As$ : As, 19.63. Found: 19.30.

**General Method for the Preparation of Bis-( $\alpha$ -hydroxybenzyl)arylarsines.**—Although aryl arsines and aromatic aldehydes condense readily in the presence of conc. hydrochloric acid to give the expected condensation products, better yields are generally obtained provided anhydrous hydrogen chloride and any convenient solvent are used and the mixture mechanically stirred at the same time. A general procedure is as follows. Two moles of aldehyde are dissolved in 5 times the weight of dry ether and dry hydrogen chloride is passed in for a few minutes. The mixture is stirred, dry carbon dioxide is, of course, passed in continuously to prevent oxidation, and one mole of aryl arsine is added. Formation of the product starts almost immediately and in many cases it separates as a solid. In the case of acetone as a solvent, the products generally do not precipitate at all. The reaction mixture is stirred for 2 or 3 hours. The precipitate is filtered, or if no precipitate is present the solvent is evaporated until the product separates. By concentrating the mother liquors a further crop of product may be obtained. There is always formed along with the normal reaction product a small

<sup>15</sup> Ref. 9, p. 2376.

amount of arylarsonic acid which is difficult to remove. It is advisable, therefore, after crystallizing the product once, to allow it to stand with dil. alkali for some time in order to dissolve out the arylarsonic acid. The product is filtered, washed with water, then, if possible, with alcohol and ether, and finally dried. A purer product is obtained by not crystallizing again after the extraction with alkali. Apparently these compounds are slightly oxidized to arylarsonic acid and aldehyde when they are in hot solution and exposed to the air. The yields vary from 40% to practically quantitative, depending largely upon the ease of purification.

The benzaldehyde derivative forms with much greater ease than the substituted benzaldehydes, the former going very smoothly.

The aromatic aldehyde condensation product also forms in the presence of a solvent and conc. hydrochloric acid, but the yields are not as satisfactory as where anhydrous hydrochloric acid is used. The substituted phenylarsine condensation products with aromatic aldehydes were made in this way before it was discovered that anhydrous hydrogen chloride worked better.

*Bis-( $\alpha$ -hydroxybenzyl)phenylarsine*,  $C_6H_5As(CHOHC_6H_5)_2$ .—This substance has been described in the preliminary article<sup>16</sup> but was made by direct addition of phenylarsine and benzaldehyde. By the process described in the general procedure, it is possible to obtain from 58 g. of benzaldehyde, 40 g. of phenylarsine, anhydrous hydrogen chloride and 300 cc. of ether, practically a quantitative yield of white, silky needles which on recrystallization from chlorobenzene melt at 193°. The product is insoluble in water, slightly soluble in hot alcohol, ether, more readily soluble in hot benzene and chlorobenzene.

*Analyses.* Subs., 0.1522, 0.1876:  $CO_2$ , 0.3704, 0.4499;  $H_2O$ , 0.0695, 0.0843. Subs., 0.1740, 0.1505: 8.7, 8.5 cc. iodine (1 cc. = 0.0041 g. As). Subs., 1.3709; naphthalene, 26.73: f. p. lowering, 0.972°. Calc. for  $C_{20}H_{19}O_2As$ : C, 65.58; H, 5.18; As, 20.49; mol. wt., 366. Found: C, 65.70, 65.41; H, 5.11, 5.01; As, 20.47, 20.43; mol. wt., 364.

*Bis-( $\alpha$ -hydroxy-*p*-chlorobenzyl)phenylarsine*,  $C_6H_5As[CHOHC_6H_4Cl(p)]_2$ .—This substance forms colorless needles from chlorobenzene melting at 164° and is more soluble in common organic solvents than the benzaldehyde compound. The yield is low (40%) since the product tends to become oily and is purified with difficulty.

*Analyses.* Subs., 0.1057: 4.3 cc. iodine (1 cc. = 0.0042 g. As). Subs., 0.1411: AgCl, 0.0905. Calc. for  $C_{20}H_{17}O_2Cl_2As$ : As, 17.24; Cl, 16.48. Found: As, 17.08; Cl, 16.65.

*Bis-( $\alpha$ -hydroxy-*p*-methoxybenzyl)phenylarsine*,  $C_6H_5As[CHOHC_6H_4OCH_3(p)]_2$ .—From 27 g. of anisaldehyde, 15 g. of phenylarsine, 200 cc. of dry ether and anhydrous hydrogen chloride, an oil is obtained after allowing the mixture to stand overnight in contact with air to oxidize any phenylarsine which has not reacted, and then evaporating the solvent at room temperature. To purify, the oil is dissolved in ether, shaken several times with aqueous sodium hydrogen sulfite and then with water, and the ethereal solution dried, filtered and evaporated. A yellowish oil results which proves by analysis to be the expected derivative. The product is insoluble in water but readily soluble in organic solvents, except petroleum ether.

<sup>16</sup> Ref. 9, p. 2377.

**Analyses.** Subs., 0.1835, 0.2013: 7.65, 8.5 cc. iodine (1 cc. = 0.0041 g. As). Calc. for  $C_{22}H_{20}O_4As$ : As, 17.61. Found: 17.09, 17.31.

**Bis-[*o*-(carboxymethoxy)- $\alpha$ -hydroxybenzyl]phenylarsine,  $C_6H_5As[CHOHC_6H_4OC-H_3CO_2H(o)]_2$ .**—From 30 g. of *o*-aldehydophenoxy-acetic acid, 13 g. of phenylarsine, 100 cc. of acetone and 1 cc. of conc. hydrochloric acid a solution is obtained which upon spontaneous evaporation (since heating in presence of hydrochloric acid causes decomposition) of the solvent yields an oil soluble in sodium hydroxide. By the concentration of the alkaline solution, an orange-brown sodium salt is obtained. This is dissolved in water and fractionally precipitated with hydrochloric acid. The first small fractions are considerably colored and are discarded. The material forms a yellowish powder which weighs 42 g. and melts at 145–147° with loss of carbon dioxide. By solution in glacial acetic acid and precipitation with water, the product may be obtained colorless.

**Analyses.** Subs., 0.2794, 0.1945: 9.8, 7.1 cc. iodine (1 cc. = 0.00446 g. As). Subs., 0.1480: 5.0 cc. 0.1187 *N* NaOH. Calc. for  $C_{24}H_{22}O_4As$ : As, 16.18; neut. equiv., 241. Found: As, 16.28, 16.27; neut. equiv., 249.

Analyses of the sodium salt (dried *in vacuo* at 100°) were also made.

**Analyses.** Subs., 0.1574, 0.1941: 4.8, 5.8 cc. iodine (1 cc. = 0.00446 g. As). Calc. for  $C_{24}H_{21}O_4AsNa_2$ : As, 13.42. Found: As, 13.59, 13.26.

### General Method for the Preparation of Tetrahydro-1,4,2,5-dioxdiarsines.

—A 150cc. Erlenmeyer flask is fitted with a 3-hole rubber stopper carrying a 50cc. separatory funnel, an inlet tube reaching nearly to the bottom of the flask and an outlet tube connected to a calcium chloride tube. The flask is filled with carbon dioxide and cooled with ice. A mole of phenylarsine is now added and a stream of dry hydrogen chloride is passed through it. At the same time that the hydrogen chloride is started, two moles of aliphatic aldehyde are added drop by drop and the stream of gas continued about half an hour after completion of the addition of the aldehyde. After standing for a day or two the reaction mixture is distilled, at first under ordinary pressure in order to remove hydrochloric acid, unchanged aldehyde and any alcohol or alcohol derivatives which have been produced in the reaction. The residual mixture is now distilled under diminished pressure and the first fraction consisting of the bis-( $\alpha$ -hydroxyalkyl)phenylarsine is obtained. The residue consists of the tetrahydro-dioxdiarsine in 50 to 90% yields. On account of the extremely high boiling point of the tetrahydro-dioxdiarsines it is difficult to obtain a large yield of purified product from the crude material. This is due to the fact that there is a partial decomposition during distillation even at pressures below 2 mm. The undistilled material, however, is practically pure as shown by analyses in several instances. These compounds from aliphatic aldehydes are practically colorless oils which are insoluble in water and soluble in the common organic solvents.

**Tetrahydro-2,5-diphenyl-1,4,2,5-dioxdiarsine,  $C_6H_5As$**    **$AsC_6H_5$ .**—This

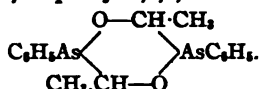
substance is obtained by mixing paraformaldehyde, phenylarsine and conc. hydrochloric acid. After shaking the reaction mixture occasionally for some time and allowing it to

stand for a few hours, it is distilled. By this method one would expect to obtain *bis*-(hydroxymethyl)phenylarsine, but this product is apparently unstable as obvious from the gradual evolution of gas during the vacuum distillation and the fact that no constant boiling point is reached until the point at which the tetrahydro-dioxdiarsine distils.

The low-boiling distillate contains methyl alcohol, as shown by the preparation of the 3,5-dinitrobenzoate which melts at 106–107°. The product after distilling twice, boils constant at 215–216° at 9 mm.;  $d_{25}^{25}$ , 1.547;  $n_D^{25}$ , 1.6522. This compound is very readily oxidized in the air and consequently all operations must be performed in an atmosphere of carbon dioxide. The yield of pure product from 15 g. of phenylarsine is about 10 g.

*Analyses.* Subs., 0.2560:  $\text{CO}_2$ , 0.4320;  $\text{H}_2\text{O}$ , 0.0970. Subs., 0.3953, 0.1617: 39.4, 16.1 cc. iodine (1 cc. = 0.0042 g. As). Subs., 0.7900: 22.0 g. benzene; f. p. lowering, 0.506°. Calc. for  $\text{C}_{16}\text{H}_{18}\text{O}_2\text{As}_2$ : C, 46.15; H, 3.85; As, 41.21; mol. wt., 364. Found: C, 46.01; H, 4.08; As, 41.81; 41.82; mol. wt. 355.

**Tetrahydro-3,6-dimethyl-2,5-diphenyl-1,4,2,5-dioxdiarsine,**

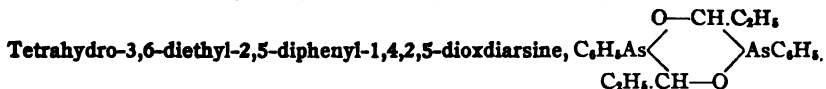


—By using the general method, a colorless oil is obtained boiling at 257° at 10 mm. with slight decomposition;  $d_{25}^{25}$ , 1.369;  $n_D^{25}$ , 1.6332.

This substance may also be obtained by heating *bis*-( $\alpha$ -hydroxyethyl)phenylarsine with half its weight of acetic anhydride under a reflux condenser in an oil-bath at 140–150° for 7 hours. The reaction mixture is carefully distilled, first at atmospheric pressure, and a portion boiling at 75–90° collected. Ethyl acetate is present in this fraction. Diminished pressure is then used and the main portion of material collected from 250–265° at 10 mm. After purification by one or more redistillations, a product boiling at the above point and with the same constants is produced.

A third method of preparation consists merely in allowing *bis*-( $\alpha$ -hydroxyethyl)phenylarsine to stand a few days in the presence of anhydrous hydrogen chloride. By obtaining the tetrahydro-dioxdiarsine on distillation of this reaction mixture, it is shown that the *bis*-( $\alpha$ -hydroxyalkyl)phenylarsine is an intermediate in the production of tetrahydro-dioxdiarsine from aldehyde and primary arsine.

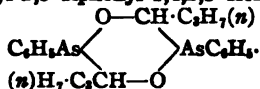
*Analyses.* Subs., 0.2158, 0.1478:  $\text{CO}_2$ , 0.3913, 0.2638;  $\text{H}_2\text{O}$ , 0.1000, 0.0668. Subs., 0.1786, 0.1577: 16.5, 14.6 cc. iodine (1 cc. = 0.0041 g. As). Subs., 0.5415: 22.0 g. benzene: f. p. lowering, 0.320°. Calc. for  $\text{C}_{18}\text{H}_{20}\text{O}_2\text{As}_2$ : C, 48.98; H, 4.59; As, 38.27; mol. wt., 392. Found: C, 48.98; 48.75; H, 5.19, 5.06; As, 37.88, 37.87; mol. wt., 384.



—This substance is readily obtained by the general method, using propionic aldehyde in slight excess and phenylarsine. The yield of crude material is practically quantitative. The substance boils at such a high point, however, that not more than 25% of pure material can be obtained by vacuum distillation, owing to the decomposition during that procedure. The distilled substance boils at 212° at 2 mm.;  $d_{25}^{25}$ , 1.336;  $n_D^{25}$ , 1.6217.

*Analyses.* Subs., 0.1173, 0.1030: 9.3, 8.2 cc. iodine (1 cc. = 0.0446 g. As). Calc. for  $\text{C}_{18}\text{H}_{20}\text{O}_2\text{As}_2$ : As, 35.71. Found: 35.45, 35.50.

**Tetrahydro-3,6-di-*n*-propyl-2,5-diphenyl-1,4,2,5-dioxdiarsine,**



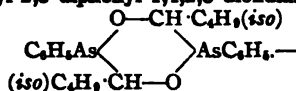


—By the general method an excellent yield of light yellow oil is produced after all the low-boiling material has been removed. This substance gave good analyses for the tetrahydro-dioxdiarsine. An attempt was made to distil the product but there was considerable decomposition during this procedure and only a small percentage could be obtained pure. The boiling point is  $241-242^{\circ}$  at 2 mm.;  $d_{25}^{25}$ , 1.297;  $n_D^{25}$ , 1.5856.

This same substance was also obtained by the action of acetic anhydride upon *bis*-( $\alpha$ -hydroxy-*n*-butyl)phenylarsine by 6 hours' refluxing. The lowest-boiling fraction is distilled under ordinary pressure and consists of a mixture of acetic anhydride and *n*-butyl acetate. Under diminished pressure a small fraction of *bis*-( $\alpha$ -hydroxy-*n*-butyl)phenylarsine comes over first. The residue after the temperature has reached  $220^{\circ}$  at 8 mm. is dissolved in acetone, the solution filtered and the filtrate evaporated *in vacuo*, thus giving a yellow oil. This consists of practically pure tetrahydro-dioxdiarsine.

*Analyses.* Subs., 0.1055, 0.1627: 8.7, 13.4 cc. iodine (1 cc. = 0.0041 g. As). Calc. for  $C_{20}H_{20}O_2As_2$ : As, 33.48. Found: 33.81, 33.77.

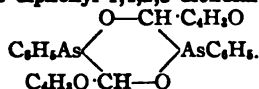
**Tetrahydro-3,6-diisobutyl-2,5-diphenyl-1,4,2,5-dioxdiarsine,**



Eight g. of phenylarsine and 9 g. of *isovaleraldehyde* are condensed by the general method with the additional procedure of vigorous agitation of the reaction mixture during the addition of aldehyde. After standing for several days the reaction mixture is distilled under diminished pressure and the portion which boils below  $240^{\circ}$  at 16 mm. discarded. The remainder is dissolved in acetone and filtered through bone-black on a folded filter. On evaporation of the filtrate in a vacuum desiccator, there remains a nearly colorless oil, weighing 5.5 g. The product is comparatively stable in air;  $d_{25}^{25}$ , 1.296;  $n_D^{25}$ , 1.5869.

*Analyses.* Subs., 0.1066, 0.1166: 7.5, 8.2 cc. iodine (1 cc. = 0.00446 g. As). Calc. for  $C_{22}H_{26}O_2As_2$ : As, 31.51. Found: 31.38, 31.37.

**Tetrahydro-3,6-difuryl-2,5-diphenyl-1,4,2,5-dioxdiarsine,**



—This substance forms with extreme ease and in quantitative yield when freshly distilled furfural and phenylarsine are mixed and a small amount of aqueous or anhydrous hydrogen chloride is added. The reaction is so violent that it is necessary to keep the mixture cooled at all times with ice and salt. The product consists of a hard mass which when powdered resembles zinc dust. It burns without melting, leaving no residue. It is insoluble in all solvents and before analysis was boiled successively with dil. alkali, water, alcohol and benzene. The same substance is formed when furfural is added drop by drop to a benzene solution of phenylarsine at  $20^{\circ}$  in the presence of conc. hydrochloric acid.

*Analyses.* Subs., 0.2557:  $\text{CO}_2$ , 0.5214;  $\text{H}_2\text{O}$ , 0.0879. Subs., 0.1477, 0.1470: 7.05, 7.1 cc. iodine (1 cc. = 0.0064 g. As). Calc. for  $C_{22}H_{18}O_4As_2$ : C, 53.23; H, 3.62; As, 30.24. Found: C, 55.61; H, 3.85; As, 30.54, 30.90.

### Para-chlorophenylarsine and Derivatives

The experimental work on the preparation of *p*-chlorophenylarsine and its derivatives was carried out by W. A. Carothers.

*p*-Chlorophenylarsonic acid,  $\text{ClC}_6\text{H}_4\text{AsO}_3\text{H}_2$ <sup>17</sup>.—A solution of 126 g. of *p*-chloroaniline in 600 cc. of water and 180 cc. of conc. hydrochloric acid is cooled to 0° and diazotized with 68 g. of sodium nitrite in 250 cc. of water, the temperature being kept constantly below 7°. A solution is made of 350 g. of technical arsenious oxide (1.8 moles) in 565 g. of sodium carbonate dissolved in 1.5 liters of water by heating on a water-bath for 2 hours with occasional shaking; if this solution is not clear, it is filtered. About 15 g. of powdered copper sulfate is now dissolved in the sodium arsenite solution and the mixture cooled to room temperature. The diazo solution is siphoned into it very slowly. During the addition, constant mechanical stirring is carried on. The speed of the addition is limited by the tendency of the reaction mixture to foam. Addition of a few cubic centimeters of benzene from time to time tends to prevent this foaming. The reaction is allowed to continue for 3 to 4 hours after the addition is complete, the mixture allowed to stand for 12 hours without stirring and then is filtered from any tarry product that may have separated. The filtrate is acidified with glacial acetic acid, the addition being made carefully in order to prevent excessive foaming in the mixture. Arsenious oxide is thus precipitated, while the *p*-chlorophenylarsonic acid remains in solution. After filtration, the latter is precipitated by the addition of conc. hydrochloric acid. It is filtered, washed with cold water and dried. A yield of from 160 to 200 g. is readily obtained (60–85%). After crystallization from alcohol the substance decomposes at about 348°. For analysis it was crystallized once from glacial acetic acid and twice from ethyl alcohol and then dried at 90° *in vacuo*.

*Analyses.* Subs., 0.1612, 0.1782, 0.1966: 26.38, 28.77, 31.60 cc. iodine (1 cc. = 0.001975 g. As). Subs., 0.4190, 0.5190: 0.2539, 0.3176 g. AgCl. Calc. for  $\text{C}_6\text{H}_4\text{O}_3\text{ClAs}$ : As, 31.75; Cl, 15.01. Found: As, 31.58, 31.99, 31.74; Cl, 14.99, 15.14.

*p*-Chlorophenylarsine,  $\text{ClC}_6\text{H}_4\text{AsH}_2$ .—The preparation of this substance is not possible by the use of the directions which are given under phenylarsine. It is necessary to use methyl alcohol instead of water. This presumably acts as a solvent and hastens the reaction. In a 3-liter round-bottom flask are placed 70 g. of *p*-chlorophenylarsonic acid, 350 g. of well amalgamated zinc dust and 250 cc. of methyl alcohol. The flask is provided with a 2-hole rubber stopper; through one hole is inserted a reflux condenser, the upper end of which is provided with a mercury trap; in the other hole is placed a 500cc. separatory funnel. Conc. hydrochloric acid is placed in this funnel and allowed to drop into the reaction mixture regularly at the rate of about 3 or 4 drops a minute. About 1 liter of acid is thus added and the reaction is considered complete when practically all the zinc has disappeared. This required, in various runs, from 3 days' to 1 weeks' time. The stopper is removed from the flask and quickly replaced by another holding 3 tubes, 2 of which extend to the bottom of the flask, 1 allowing for the entrance of steam, the second for carbon dioxide, and the third tube is attached to a condenser set for downward distillation. The receiver at the end of the condenser consists of a suction flask attached tightly by means of an adapter to the condenser. The whole apparatus is filled with carbon dioxide, and a slow stream of carbon dioxide is continued while steam is blown into the reaction mixture. The *p*-chlorophenylarsine distills with the water and methyl alcohol, and occasionally solidifies in the condenser. When no more arsine distills, the stopper holding the adapter leading to the receiver is removed and replaced by one carrying a right-angle tube through which carbon dioxide is conducted. The *p*-chlorophenylarsine remains in the bottom of the receiver as a dark solid. By using care, a considerable portion of the water and dilute alcohol above the arsine can be poured from the side arm of the suction flask receiver, allowing the carbon dioxide to enter at the same time. The stopper holding the tube through which

<sup>17</sup> This compound has been previously made by the diazotization of arsanilic acid and replacement of the diazo group by chlorine; *Ber.*, 41, 1856 (1908).

the carbon dioxide enters is partially removed, and 200 cc. of ether added. The side-tube of this suction flask is now inserted in the mouth of a 500cc. separatory funnel filled with carbon dioxide and the ether layer containing the *p*-chlorophenylarsine forced into it by means of a stream of carbon dioxide. Washing the aqueous distillate with one or two portions of ether is advisable. Any water may be separated from the ether solution which is thus obtained, after which it is dried over solid potassium hydroxide. The ether solution is transferred to a vacuum distilling flask as follows. A funnel containing the ether solution is inserted through a 2-hole rubber stopper which closes the main neck of the Claisen flask. The usual capillary tube is extended through the other opening and a carbon dioxide cylinder is attached. The apparatus is evacuated several times and filled with carbon dioxide in order that all the air may be removed. Finally, it is evacuated and the stopcock of the separatory funnel opened to allow the ether solution to enter the Claisen flask. The ether is removed and the *p*-chlorophenylarsine distils. After one or sometimes two redistillations, it is absolutely pure and then boils at 116° at 33 mm., or 159° at 200 mm. It melts at 30.5–30.7°, forming thin, transparent leaves sometimes as large as 1.5 cm. square. The yield, after complete purification, varies from 16 to 26 g.;  $d_{25}^{25}$ , 1.507;  $n_D^{25}$ , 1.6143.

*Analyses.* Subs., 0.5147, 0.3622: 103.64, 72.20 cc. iodine (1 cc. = 0.001975 g. As). Subs., 0.4259, 0.4592, 0.2539: 0.3184, 0.3520, 0.1914 g. AgCl. Calc. for  $C_6H_4ClAs$ : Cl, 18.81; As, 39.79. Found: As, 39.75, 39.37; Cl, 18.50, 18.97, 18.65.

*Bis-( $\alpha$ -hydroxybenzyl)-p-chlorophenylarsine*,  $ClC_6H_4As(CHOHC_6H_5)_2$ .—One mole of arsine and 2 moles of aldehyde are mixed and a small amount of conc. hydrochloric acid is added. Within a half hour, the whole mass sets to an amorphous solid. On standing for an hour, even in an atmosphere of carbon dioxide, it is found to have completely changed to a canary-yellow color. By extracting the reaction mixture with hot chlorobenzene, there crystallize from this solvent long, white, silky needles which can be purified from a mixture of chlorobenzene and alcohol and then melt at 218–218.5°. The yield is small. Moreover, analysis indicates the product at hand is not quite pure in spite of careful crystallization. The chlorobenzene-insoluble residue consists of a bright yellow, sticky mass containing benzaldehyde; after standing in the air, however, this becomes dry and on long standing lighter colored, and finally is found to consist chiefly of *p*-chlorophenylarsonic acid.

*Analyses.* Subs., 0.1082, 0.1144: 8.95, 9.21 cc. iodine (1 cc. = 0.001975 g. As). Subs., 0.1406, 0.1676: 0.0473, 0.0558 g. AgCl. Calc. for  $C_{12}H_{10}O_2ClAs$ : As, 18.72; Cl, 8.85. Found: Cl, 8.32, 8.23; As, 16.34, 15.90.

*Bis-( $\alpha$ -hydroxyethyl)-p-chlorophenylarsine*,  $ClC_6H_4As(CHOHCH_3)_2$ .—This substance is obtained in the usual way and when pure is a colorless oil boiling at 183° at 23 mm.;  $d_{25}^{25}$ , 1.336;  $n_D^{25}$ , 1.5728.

*Analyses.* Subs., 0.3674, 0.3771: 50.01, 52.18 cc. iodine (1 cc. = 0.001975 g. As). Subs., 0.3215, 0.3601: 0.1620, 0.1820 g. AgCl. Calc. for  $C_{10}H_{14}O_2ClAs$ : Cl, 12.82; As, 27.12. Found: Cl, 12.47, 12.50; As, 26.88, 27.33.

### Ortho-chlorophenylarsine and Derivatives

The experimental work on the preparation of *o*-chlorophenylarsine and its derivatives was carried out by E. E. Parks.

*o*-Chlorophenylarsonic acid,  $ClC_6H_4AsO_2H_2$ .—This acid is prepared according to the same general directions as used for *p*-chlorophenylarsonic acid. The crude material forms in yields varying from 60 to 75%. It is readily purified by crystallization from hot water or dilute alcohol and then melts at 186–187°. The acid is dried for 1 hour at 100° before analysis.

*Analyses.* Subs., 0.2595: 18.5 cc. of iodine (1 cc. = 0.00446 g. As). Calc. for  $C_6H_5O_2ClAs$ : As, 31.75. Found: 31.83.

*o*-Chlorophenylarsine,  $ClC_6H_4AsH_2$ .—This substance is prepared by the general directions used for phenylarsine except that no ether is used and after the reduction is complete the *o*-chlorophenylarsine is distilled with steam from the reaction mixture. In this preparation it is not necessary to use methyl alcohol as described under *p*-chlorophenylarsine. The product boils at  $206^\circ$  at atmospheric pressure and forms in yields of 45 to 60%;  $d_{25}^{25}$ , 1.519;  $n_D^{25}$ , 1.6250.

*Analyses.* Subs., 0.1206: 10.75 cc. iodine (1 cc. = 0.00446 g. As). Calc. for  $C_6H_5ClAs$ : As, 39.79. Found: 39.75.

*Bis-( $\alpha$ -hydroxybenzyl)-o-chlorophenylarsine*,  $ClC_6H_4As(CHOHC_6H_5)_2$ .—This substance is readily produced in the usual way by the action of *o*-chlorophenylarsine upon benzaldehyde. It forms white crystals which are readily crystallized from either ether or alcohol. When pure it melts at  $146$ – $147^\circ$ . The analyses on this product are low unless the product is heated to  $110$ – $120^\circ$  for one-half to one hour. Under these conditions the product seems to fuse slightly and turn a trifle brown, but gives correct analyses for the product at hand and, on recrystallizing, it is found that no decomposition has taken place. It seems probable that this substance holds tenaciously the alcohol from which it is crystallized and only by heating to  $120^\circ$  is this removed.

*Analyses.* Subs., 0.2894, 0.3558: 6.63, 8.61 cc.  $AgNO_3$  (1 cc. = 0.003722 g. Cl). Calc. for  $C_{18}H_{15}O_2ClAs$ : Cl, 8.85. Found: 8.53, 9.00.

### Para-tolylarsine and Derivatives

The experimental work on *p*-tolylarsine and its derivatives was carried out by G. O. Burr.

*p*-Tolylarsonic acid,<sup>18</sup>  $CH_3C_6H_4AsO_3H_2$ .—A solution is made of 214 g. of *p*-toluidine in 2 liters of water and 5 moles of hydrochloric acid. The temperature is reduced to  $0^\circ$  and 2 moles of sodium nitrite in conc. aqueous solution is added drop by drop from a separatory funnel. During the addition, the solution should be mechanically stirred. One and two-tenths moles of arsenious oxide is dissolved in a solution of slightly more than 4 moles of sodium carbonate in a liter of water. The solution is heated for some time but does not become clear; 20 g. of crystallized copper sulfate is dissolved in this solution, which is then cooled to  $17^\circ$ . At this point the cold diazo solution is siphoned slowly into the arsenite (45 minutes) and the reaction mixture then stirred for 12 hours. Tar separates which is filtered, and the filtrate is acidified with hydrochloric acid. *p*-Tolylarsonic acid is precipitated as a white powder and may be purified by crystallization from water. The yield varies from 50 to 65%.

*p*-Tolylarsine,  $CH_3C_6H_4AsH_2$ .—The same procedure is used in the preparation of this substance as in the preparation of phenylarsine but the use of a slightly greater amount of zinc is desirable. The product is a colorless liquid boiling at  $113.5^\circ$  at 44 mm. It crystallizes in white, shiny plates which melt at  $20^\circ$ . The yields vary from 30 to 50%;  $d_{25}^{25}$ , 1.295;  $n_D^{25}$ , 1.5891.

*Analyses.* Subs., 0.1670;  $CO_2$ , 0.3045;  $H_2O$ , 0.0776. Calc. for  $C_7H_9As$ : C, 50.00; H, 5.36. Found: C, 49.74; H, 5.20.

*Bis-( $\alpha$ -hydroxybenzyl)-p-tolylarsine*,  $CH_3C_6H_4As(CHOHC_6H_5)_2$ .—This is prepared in the same manner as is the phenyl derivative, but is not produced in so good yields.

<sup>18</sup> This substance has been previously made by the hydrolysis of *p*-tolyl-phenylarsenious chloride; *Ann.*, 320, 303 (1902); 201, 256 (1880); also by the action of sodium toluene-*isodiazotate* on sodium arsenite; Ger. pat. 250,264.

It forms long, white needles which after crystallization from a mixture of benzene and alcohol melt at 208°.

*Analyses.* Subs., 0.2185: CO<sub>2</sub>, 0.5280; H<sub>2</sub>O, 0.0940. Calc. for C<sub>22</sub>H<sub>22</sub>O<sub>2</sub>As: C, 66.14, H, 5.51. Found: C, 65.92; H, 4.83.

Subs., 0.2033, 0.2031: 18.37, 18.27 cc. iodine (1 cc. = 0.00206 g. As). Calc. for C<sub>22</sub>H<sub>22</sub>O<sub>2</sub>As: As, 19.73. Found: 18.55, 18.53.

*Bis-(α-hydroxyethyl)-p-tolylarsine*, CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>As(CHOHCH<sub>3</sub>)<sub>2</sub>.—A mixture of paraldehyde and arsine with a few drops of hydrochloric acid is allowed to stand for 15 hours. After working up in the usual way, the product is distilled and then gives an 80% yield of a colorless oil boiling at 176–177° at 22 mm; d<sub>25</sub><sup>18</sup>, 1.2331; n<sub>D</sub><sup>20</sup>, 1.5570. On exposure to air it oxidizes readily.

*Analyses.* Subs., 0.1438: CO<sub>2</sub>, 0.2682; H<sub>2</sub>O, 0.0809. Subs., 0.1862: 25.47 cc. iodine (1 cc. = 0.00216 g. As). Calc. for C<sub>11</sub>H<sub>17</sub>O<sub>2</sub>As: C, 51.56; H, 6.64; As, 29.30. Found: C, 50.88; H, 6.30; As, 29.54.

### Ortho-tolylarsine and Derivatives

The experimental work on *o*-tolylarsine and its derivatives was carried out by J. S. Pierce.

*o*-Tolylarsonic acid,<sup>19</sup> CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>AsO<sub>2</sub>H<sub>2</sub>.—The procedure used in the preparation of this substance is approximately the same as for the *p*-tolylarsonic acid. The yield, however, is considerably lower on account of the greater solubility and amounts in general to not over about 40%. The melting point is 159–160°, which agrees with that given in the literature.

*o*-Tolylarsine, CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>AsH<sub>2</sub>.—This product is made in the same way as phenylarsine. The product is a colorless oil boiling at 121° at 93 mm; d<sub>25</sub><sup>25</sup>, 1.301; n<sub>D</sub><sup>26</sup>, 1.5925.

*Analyses.* Subs., 0.1925, 0.2342: 24.13, 29.61 cc. iodine (1 cc. = 0.003515 g. As). Calc. for C<sub>7</sub>H<sub>9</sub>As: As, 44.60. Found: 44.06, 44.44.

On exposure to air the arsine oxidizes rapidly to the arseno compound which can be separated from traces of admixed arsonic acid by sodium hydroxide. By crystallization from benzene a pure sample was obtained melting at 205–208°.

*Analysis.* Subs., 0.1530: 20.18 cc. iodine (1 cc. = 0.003515 g. As). Calc. for C<sub>7</sub>H<sub>11</sub>As: As, 45.14. Found: 46.36.

*Bis-(α-hydroxybenzyl)-o-tolylarsine*, CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>As(CHOHC<sub>6</sub>H<sub>5</sub>)<sub>2</sub>.—The product is purified by crystallization from ether, forming white, needle-like crystals which melt at 140°.

*Analyses.* Subs., 0.0596, 0.0488: 3.29, 2.68 cc. iodine (1 cc. = 0.003515 g. As). Calc. for C<sub>21</sub>H<sub>21</sub>O<sub>2</sub>As: As, 19.71. Found: 19.40, 19.30.

*Bis-(α-hydroxyethyl)-o-tolylarsine*, CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>As(CHOHCH<sub>3</sub>)<sub>2</sub>.—This is a colorless oil boiling at 165° at 21 mm.; d<sub>25</sub><sup>25</sup>, 1.244; n<sub>D</sub><sup>30</sup>, 1.5573. This substance has a slightly greater tendency to oxidize than other analogous compounds, so it should be kept in an atmosphere of carbon dioxide. The ease of decomposition probably accounts for the low analysis.

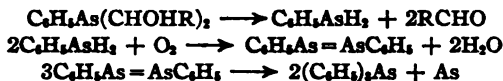
*Analyses.* Subs., 0.0974, 0.1527: 7.67, 12.04 cc. iodine (1 cc. = 0.003528 g. As). Calc. for C<sub>11</sub>H<sub>17</sub>O<sub>2</sub>As: As, 29.25. Found: 27.78, 27.82.

### Reactions of the Condensation Products, C<sub>6</sub>H<sub>5</sub>As(CHOHR)<sub>2</sub>

**Stability.**—When heated strongly over a free flame, the substances

<sup>19</sup> The product has previously been made by the hydrolysis of *o*-tolylarsenious chloride; *Ann.*, 201, 255 (1880).

are decomposed into aldehyde and phenylarsine. The latter is immediately oxidized to arsenobenzene in the presence of air. Arsenobenzene is changed completely into triphenylarsine, m. p. 58°, and free arsenic.<sup>20</sup> The following reactions are indicated for the heat decomposition.



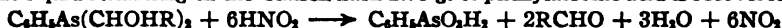
The products are perfectly stable in long continued contact with water, dil. sodium hydroxide and cold dil. hydrochloric acid.

When 5 g. of *bis*-( $\alpha$ -hydroxy-*n*-butyl)phenylarsine is mixed with 25 cc. of water and sealed in a bomb tube, the lower end of which is immersed in an oil-bath heated at 140° for 30 hours, it is unchanged. In a similar manner 1 g. of *bis*-( $\alpha$ -hydroxybenzyl)phenylarsine is recovered unchanged in weight and melting point after 65 hours' heating. *Bis*-( $\alpha$ -hydroxy-*n*-butyl)phenylarsine and *bis*-( $\alpha$ -hydroxybenzyl)phenylarsine are unaffected by 24 hours' heating with 10% sodium hydroxide solution. On the other hand, heating for only a short time with dil. hydrochloric acid is sufficient to cause decomposition. This reaction is discussed under the heading "Halogen Acids."

**Oxidation.**—When the *bis*-( $\alpha$ -hydroxyalkyl)arylsarsines are allowed to stand for a few days in contact with the air a white solid is gradually deposited. The liquid portion is found to have lost arsenic and to give a strong fuchsin aldehyde test. The solid is identified as the respective aryl arsonic acid. This oxidation is more rapid in solution, particularly in carbon tetrachloride.

Thus 1 g. of *bis*-( $\alpha$ -hydroxyethyl)phenylarsine is completely decomposed by dissolving it in 10 cc. of carbon tetrachloride and passing a slow stream of air through the solution for 1 hour. Heat is evolved, the solution becomes turbid, and the odor of phosgene is very distinct. The mixture gives a strong aldehyde test and on evaporation phenylarsonic acid is the only substance obtained. No action is observed when a stream of carbon dioxide is substituted for air. *Bis*-( $\alpha$ -hydroxy-*n*-butyl)phenylarsine is oxidized in exactly the same way, but *bis*-( $\alpha$ -hydroxybenzyl)phenylarsine is perfectly stable in carbon tetrachloride solution.

In a 50cc. Claisen flask connected to a spiral condenser and receiver, both cooled by ice and water, is placed 5 g. of *bis*-( $\alpha$ -hydroxy-*n*-butyl)phenylarsine. Through a separatory funnel 18 cc. of 35% nitric acid is now added drop by drop. A vigorous reaction takes place. The distillate, weighing 2 g., is butyraldehyde. On evaporation of the liquid remaining in the Claisen flask 2.75 g. of phenylarsonic acid is recovered.



Alkaline potassium permanganate gives a similar result. The same reactions occur when *bis*-( $\alpha$ -hydroxyethyl)phenylarsine is treated with nitric acid or potassium permanganate.

**Reduction.**—A number of attempts have been made to reduce *bis*-( $\alpha$ -hydroxyethyl)phenylarsine  $\text{C}_6\text{H}_5\text{As}(\text{CHOHCH}_3)_2$ , to phenyldiethyl arsine,  $\text{C}_6\text{H}_5\text{As}(\text{CH}_2\text{CH}_3)_2$ . Zinc and hydrochloric acid, zinc and acetic acid, aluminum powder and sodium hydroxide and sodium and absolute alcohol do not reduce this compound, the original substance being recovered in

<sup>20</sup> *Ber.*, 14, 913 (1881).

each case. In the first three instances the condensation product appears to coat the metal so that the latter reacts with great difficulty.

**Dehydration.**—When a solution of *bis*-( $\alpha$ -hydroxyethyl)phenylarsine in dry ether is allowed to stand with phosphorus pentoxide, slight charring occurs but most of the product is recovered unchanged. Fused zinc chloride dissolves in the same compound with formation of a thick sirup, probably an addition product.

Ten g. of *bis*-( $\alpha$ -hydroxyethyl)phenylarsine and 2 g. of metallic sodium are placed in a small beaker and allowed to stand in a desiccator over sulfuric acid for 2 weeks. During that time the sodium becomes discolored, but the unchanged condensation product can be recovered by dissolving in dry ether, filtering, and distilling the filtrate.

**Halogens.**—Two moles of solid iodine are placed in the apparatus which has been described in connection with oxidation by nitric acid. One mole of *bis*-( $\alpha$ -hydroxy-*n*-butyl)phenylarsine is added drop by drop. The liquid which distils over below  $80^{\circ}$  is butyraldehyde. A heavy, dark oil remaining in the Claisen flask cannot be distilled under 20 mm. pressure without decomposition. It gives free iodine and phenylarsonic acid when treated with conc. nitric acid. This behavior is characteristic of phenylarsenious iodide.<sup>20</sup> Other condensation products give similar results.



The aliphatic aldehyde compounds may be dissolved in ether and titrated quantitatively with standard iodine solution as represented in the above equation. The end-point is reached when the ether solution assumes a permanent yellow color. The results indicate the absorption of 4 atoms of iodine to 1 molecule of arsine. After neutralization of the ether solution at the end of titration, a strong fuchsin aldehyde test is obtained.

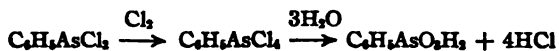
*Bis*-( $\alpha$ -hydroxy-*n*-propyl)phenylarsine: subs., 0.1208: 16.1 cc. of iodine (1 cc. = 0.0164 g. I). Calc. for  $\text{C}_{12}\text{H}_{18}\text{O}_2\text{As}$ : 16.05 cc.

*Bis*-( $\alpha$ -hydroxy-*n*-butyl)phenylarsine: subs., 0.1383: 16.3 cc. iodine (1 cc. = 0.0164 g. I). Calc. for  $\text{C}_{14}\text{H}_{22}\text{O}_2\text{As}$ : 16.48 cc.

Bromine reacts violently leaving a heavy reddish oil. Since the latter gives phenylarsonic acid and free bromine when treated with nitric acid, it is probably phenyl-dibromo-arsine. The reaction doubtless follows the same course as with iodine, although the formation of aldehyde has not been proved.

A stream of moist chlorine is passed into several grams of *bis*-( $\alpha$ -hydroxyethyl)phenylarsine. A violent reaction accompanied by considerable decomposition takes place. On cooling, needles form which have been identified after recrystallization from alcohol as phenylarsonic acid. It is concluded that the reaction followed a course similar to that given by iodine, phenyl-dichloro-arsine being formed. The production of phenylarsonic acid is explained as follows.<sup>21</sup>

<sup>21</sup> *Ber.*, 9, 1568 (1876).



It is noteworthy that the *bis*-( $\alpha$ -hydroxyalkyl)arylsarsines do not form addition products with chlorine as do the isomeric esters<sup>22</sup> of phenylarsenious acid.

**Ethyl Iodide.**—Three g. of *bis*-( $\alpha$ -hydroxyethyl)phenylarsine and 2 g. of ethyl iodide, when sealed in a test-tube and allowed to stand for 6 months, form gradually a dark sirupy mass which cannot be purified.

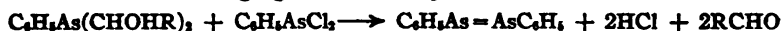
Six g. of *bis*-( $\alpha$ -hydroxy-*n*-butyl)phenylarsine and 4 g. of ethyl iodide are refluxed gently for 20 hours. The solution is transferred to a crystallizing dish and evaporated spontaneously. The residue consists of phenylarsine oxide, m. p. 120–122°. The same product is obtained when *bis*-( $\alpha$ -hydroxybenzyl)phenylarsine is used in this reaction.

**Phosphorus Pentachloride.**—Thirty-five g. of phosphorus pentachloride is placed in a small Claisen flask connected to a glass worm condenser, which is cooled by a freezing mixture, and 20 g. of *bis*-( $\alpha$ -hydroxyethyl)phenylarsine is added slowly through a dropping funnel. The heat of the reaction is great but immersion of the Claisen flask in ice water holds back any material from the distillate which boils above 60°. Five g. of low-boiling product is collected; on decomposition with water (added drop by drop) practically all goes into solution and on neutralization of the latter a strong aldehyde test is obtained. The few immiscible drops are undoubtedly ethylidene chloride. The distillation is continued under diminished pressure. A fraction boiling below 60° at 80 mm., (31 g.) consists mainly of phosphorus trichloride. The fraction (16 g.), boiling at 153–155° at 18 mm., is phenylarsenious chloride.

Subs., 0.2127: 11.0 cc. iodine (1 cc. = 0.0064 g. As). Subs., 0.1663: AgCl, 0.2173. Calc. for  $\text{C}_6\text{H}_5\text{Cl}_2\text{As}$ : As, 33.63; Cl, 31.84. Found: As, 33.57; Cl, 32.29.



**Phenylarsenious Chloride.**—One g. of *bis*-( $\alpha$ -hydroxyethyl)phenylarsine is mixed with an equal weight of phenylarsenious chloride. Slight warming and turbidity are observed. After 1 week the mixture is practically solid. It is transferred to a filter and washed thoroughly with ether. The residue is arsenobenzene, identified by a mixed melting point at 196–199°. The washings give an aldehyde test.



**Acid Chlorides.**—Many attempts to prepare esters from all of the simple condensation products by means of acetyl chloride, acetic anhydride, oxalyl bromide, oxalyl chloride, benzoyl chloride and *p*-nitrobenzoyl chloride have been made. In the cold without solvent (except in the case of oxalyl chloride which acts as a chlorinating agent in the manner of phosphorus pentachloride), in the Schotten-Baumann reaction and in

<sup>22</sup> *Ann.*, 320, 1287 (1902).



pyridine solution the compounds are unaffected. The result of heating certain of these substances with acid chlorides or anhydrides is discussed under the preparation of tetrahydro-dioxdiarsines.

**Grignard Reagents.**—The substances do not give any apparent reaction with methyl magnesium iodide in dry ether solution. Using the method of Zerewitinoff,<sup>22</sup> there is no evidence of reaction with methyl magnesium iodide in *n*-butyl ether either at room temperature or 150°.

**Halogen Acids.**—When constant-boiling hydriodic acid is added to *bis*-( $\alpha$ -hydroxyethyl)phenylarsine, heat is evolved, the acid is decolorized and a yellow solid is formed within a few minutes. The product, filtered off and washed with ether, is a yellow powder, m. p. 94–96°, insoluble in water, slightly soluble in organic solvents. It is stable to alkali, but soon melts in the air to a pasty mass. It is therefore advisable to analyze immediately without any attempt at purification. The results show the formation of an addition compound between 1 mole of arsine and 1 mole of hydriodic acid.

Subs., 0.3208: 15.0 cc. iodine (1 cc. = 0.0446 g. As). Calc. for  $C_{10}H_{12}O_2As.HI$ : As, 20.27. Found: 20.85.

*Bis*-( $\alpha$ -hydroxy-*n*-butyl)phenylarsine forms an addition product with hydriodic acid, m. p. 157–158°. If too much hydriodic acid is used decomposition may take place rather than addition.

Hydrobromic acid adds much more slowly than hydriodic acid and the products are somewhat more stable. *Bis*-( $\alpha$ -hydroxyethyl)phenylarsine hydrobromide, m. p. 117–118°; *bis*-( $\alpha$ -hydroxy-*n*-butyl)phenylarsine hydrobromide, m. p. 111–112°. All of the above melting points were obtained by inserting the capillary in the bath heated to about 5° below the melting point and raising the temperature very slowly.

Some solid is formed when *bis*-( $\alpha$ -hydroxyethyl)phenylarsine is allowed to stand for several weeks with constant-boiling hydrochloric acid, but the principal reaction is decomposition.

*Bis*-( $\alpha$ -hydroxybenzyl)phenylarsine does not form addition compounds with any of the halogen acids even on long standing.

**Addition Compounds with Chloroplatinic Acid.**—When treated in alcoholic solution with a slight excess of chloroplatinic acid, the *bis*-( $\alpha$ -hydroxyalkyl)arylarsines form addition compounds in 1:1 proportion. By addition of water, the product is thrown down as a flocculent precipitate. After several crystallizations from dil. alcohol, the substances are finally pure. In final form they are light yellow powders. The following have been prepared.

*Bis*-( $\alpha$ -hydroxyethyl)phenylarsine chloroplatinate,  $C_{10}H_{12}As(CHOHCH_2)_2.H_2PtCl_6$ .—M. p., 169–170°.

<sup>22</sup> Zerewitinoff, *Ber.*, 40, 2023 (1907); 41, 2233 (1908).

*Analysis.* Subs., 0.1372: Pt, 0.0408. Calc. for  $C_{10}H_{11}O_2As.H_2PtCl_6$ : Pt, 29.91. Found: 29.73.

*Bis-( $\alpha$ -hydroxy-*n*-propyl)phenylarsine chloroplatinate*,  $C_6H_5As(CHOHC_2H_5)_2.H_2PtCl_6$ .—M. p., 148–149°.

*Analysis.* Subs., 0.2942: Pt, 0.0824. Calc. for  $C_{13}H_{19}O_2As.H_2PtCl_6$ : Pt, 28.66. Found: 28.01.

*Bis-( $\alpha$ -hydroxy-*n*-butyl)phenylarsine chloroplatinate*,  $C_6H_5As(CHOHC_2H_7)_2.H_2PtCl_6$ .—M. p., 119–121°.

*Analysis.* Subs., 0.3024: Pt, 0.0822. Calc. for  $C_{14}H_{21}O_2As.H_2PtCl_6$ : Pt, 27.54. Found: 27.17.

*Bis-( $\alpha$ -hydroxyisovaleryl)phenylarsine chloroplatinate*,  $C_6H_5As(CHOHC_4H_9)_2.H_2PtCl_6$ .—M. p., 84–85°.

*Analysis.* Subs., 0.4109: Pt, 0.1086. Calc. for  $C_{18}H_{27}O_2As.H_2PtCl_6$ : Pt, 26.53. Found: 26.43.

### Reactions of the Tetrahydro-dioxdiarsines

Unless otherwise designated, the technique for the work described below is the same as that employed for the corresponding reactions of the compounds  $C_6H_5As(CHOHR)_2$ .

**Stability.**—The methyl compound is unaffected by long standing in the cold with water, dil. hydrochloric acid or dil. sodium hydroxide. Twenty g. of the same product is recovered unchanged after heating for 3 hours under a reflux condenser with a solution of 10 g. of potassium hydroxide in 50 cc. of absolute alcohol. This result is distinctly favorable to the symmetrical tetrahydro-dioxdiarsine structure which has been advanced. The compound,<sup>24</sup>  $(C_6H_5)_2AsOC_6H_5$ , is less easily hydrolyzed than the esters<sup>10</sup> of phenylarsenious acid. The tetrahydro-dioxdiarsine structure successfully explains the still greater stability which has been observed.

**Oxidation.**—The first member of the series, tetrahydro-2,5-diphenyl-1,4,2,5-dioxdiarsine, is oxidized very rapidly by air. A solution of 17 g. of the substance in 50 cc. of acetone warms on exposure to air and soon gives a strong fuchsin aldehyde test. After standing for some hours, the acetone is evaporated and the white, microcrystalline residue weighing 16 g. is recrystallized from alcohol. Although the resulting product gives a melting point about 10° below that of pure phenylarsine oxide, m. p. 119–120°, analysis provides a complete identification.

Subs., 0.2611, 0.1577:  $CO_2$ , 0.3980, 0.2410;  $H_2O$ , 0.0752, 0.0451. Subs., 0.1649: 16.6 cc. iodine (1 cc. = 0.00446 g. As). Calc. for  $C_6H_5OAs$ : C, 42.86; H, 2.98; As, 44.64. Found: C, 41.67, 41.63; H, 3.22, 3.19; As, 44.89.

The higher members of the series are oxidized much more slowly and in a number of cases the oxide obtained has a correct melting point.

When 1 g. of methyl compound is treated with conc. nitric acid, aldehyde

<sup>24</sup> *Ann.*, 321, 143 (1902).

is evolved, and phenylarsonic acid is obtained by evaporation of the reaction mixture.



**Iodine.**—One g. of methyl compound is dissolved in a few cubic centimeters of ether and iodine is added in small portions. The solution gives an aldehyde test. On evaporation there remains a heavy, dark oil, which is washed with ether by decantation and shown to be phenylarsine diiodide by a method described above.

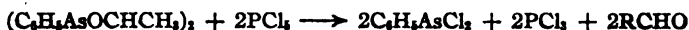


The tetrahydro-dioxdiarsines cannot be titrated quantitatively with iodine solution.

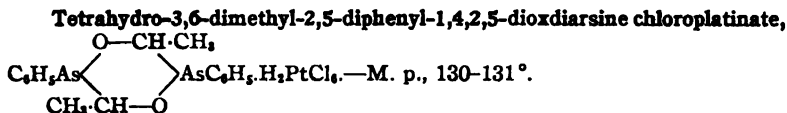
**Halogen Acids.**—Constant-boiling halogen acids do not form addition products. Slow decomposition takes place with production of aldehyde. No attempt has been made to identify other products of the reaction.

**Ethyl Iodide.**—Two g. of methyl compound and a considerable excess of ethyl iodide are refluxed for 4 hours. On evaporation of the ethyl iodide, the original tetrahydro-dioxdiarsine is recovered unchanged and practically quantitatively.

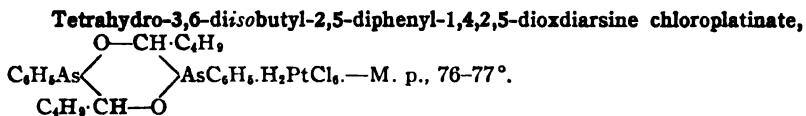
**Phosphorus Pentachloride.**—An excess of phosphorus pentachloride is mixed with 1 g. of the methyl derivative. A vigorous reaction with evolution of aldehyde takes place. The reaction mixture is treated cautiously with water and the precipitated oil removed by a capillary pipet. It yields phenylarsonic acid on treatment with chlorine and water and so is undoubtedly phenyl-dichloro-arsine.<sup>21</sup>



**Addition Compounds with Chloroplatinic Acid.**—These are prepared in the same manner as the similar substances from the di- $\alpha$ -hydroxy-alkyl arsines. The compounds crystallize in colorless flocks from dil. alcohol.



*Analysis.* Subs., 0.1069: Pt, 0.0258. Calc. for  $C_{16}H_{18}O_2As_2 \cdot H_2PtCl_6$ : Pt, 24.31. Found: 24.14.

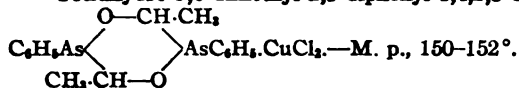


*Analysis.* Subs., 0.1338: Pt, 0.0292. Calc. for  $C_{24}H_{30}O_2As_2 \cdot H_2PtCl_6$ : Pt, 22.01. Found: 21.82.

**Addition Compounds with Cupric Chloride.**—In a similar manner to the above there are obtained addition products with cupric chloride.

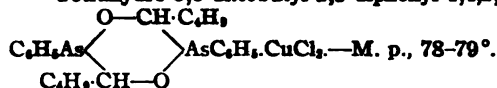
These crystallize in colorless flocks from dil. alcohol. The cuprichlorides turn green on standing in air and decompose rather quickly at 110°.

**Tetrahydro-3,6-dimethyl-2,5-diphenyl-1,4,2,5-dioxdiarsine cuprichloride,**



*Analyses.* Subs., 0.1970, 0.2010: 11.6, 11.8 cc. iodine (1 cc.=0.00446 g. As). Calc. for  $\text{C}_{18}\text{H}_{18}\text{O}_2\text{As}_2 \cdot \text{CuCl}_2$ : As, 26.59. Found: 26.25, 26.22.

**Tetrahydro-3,6-diisobutyl-2,5-diphenyl-1,4,2,5-dioxdiarsine cuprichloride,**



*Analyses.* Subs., 0.1415, 0.1730: 8.2, 9.5 cc. iodine (1 cc.=0.00446 g. As). Calc. for  $\text{C}_{22}\text{H}_{26}\text{O}_2\text{As}_2 \cdot \text{CuCl}_2$ : As, 24.57. Found: 24.71, 24.55.

### Reduction Reactions

**Benzaldehyde.**—A mixture of 7.5 g. of phenylarsine, 5 g. of benzaldehyde and 25 cc. of glacial acetic acid is heated under a reflux condenser in a current of carbon dioxide for 2 hours. The precipitated solid is filtered off, washed with ether and identified as arsenobenzene (6.75 g.). This and many other samples of arsenobenzene which have been obtained contain a slight impurity of phenylarsonic acid. The very high melting anhydride of the latter, which is formed above 158°, causes the arsenobenzene to melt as much as 25° *high*. By extraction with aqueous alkali and one or more recrystallizations from benzene or chlorobenzene, a melting point<sup>20</sup> and mixed melting point of 196–197° can be obtained.

Subs., 0.2466: 28.6 cc. iodine (1 cc.=0.0042 g. As). Calc. for  $\text{C}_{12}\text{H}_{10}\text{As}_2$ : As, 49.33. Found: 49.24.

The filtrate from the arsenobenzene has a very strong ester odor. On distillation, acetic acid is recovered at first. A fraction is collected which boils at 200–210° under atmospheric pressure. This is refluxed for several hours with conc. sodium hydroxide solution. The reaction mixture is distilled with steam, the non-aqueous portion of the distillate separated and identified as benzyl alcohol by preparation of the *p*-nitrobenzoate,<sup>25</sup> m. p. 84–88°. A portion of the residue which remains in the distilling flask is evaporated to dryness and the presence of acetic acid shown by the cacodyl test.



Phenylarsine is oxidized in a similar manner when heated at 100° with benzaldehyde in 1:1 proportion in a sealed tube filled with carbon dioxide. The reduction takes place even in the presence of conc. hydrochloric acid, the condensation reaction being entirely prevented at 100°.

<sup>20</sup> *Ber.*, 30, 2288 (1897).

**Anisic Aldehyde.**—A mixture of 6.5 g. of anisic aldehyde, 7.5 g. of phenylarsine and 5 g. of fused sodium acetate is sealed in a bomb tube filled with carbon dioxide. After 6 hours' heating on the boiling water-bath, the tube is opened, the contents filtered and the residue washed with absolute alcohol. The filtrate and washings are set aside to evaporate, and the residue washed with water to remove sodium acetate. There remains undissolved only arsenobenzene (dry weight, 6 g.).

On evaporation of the alcohol washings, an oil is obtained. It is heated under a reflux condenser with conc. sodium hydroxide solution for 2 hours and then distilled with steam from the reaction mixture. In this way anisic alcohol,<sup>26</sup> m. p. 45°, is isolated.



***p*-Chlorobenzaldehyde.**—Nine g. of *p*-chlorobenzaldehyde and 10 g. of phenylarsine are dissolved in 75 cc. of benzene, 1 g. of fused zinc chloride is added, and the mixture allowed to stand for 5 days in a sealed flask filled with carbon dioxide. The flask is opened and the arsenobenzene (dry weight, 10 g.) filtered off. On concentration of the filtrate, long prisms crystallize, m. p. 70–71°, weight, 9 g. This is *p*-chlorobenzyl alcohol.<sup>27</sup>

Subs., 0.1216: AgCl, 0.1258. Calc. for  $\text{C}_7\text{H}_7\text{OCl}$ : Cl, 24.84. Found: 25.59.

***m*-Nitrobenzaldehyde.**—When attempts are made to condense *m*-nitrobenzaldehyde and phenylarsine by the general method, a thick sirup is formed. Crystals can be obtained from this product with considerable difficulty. These are invariably arsenobenzene. Apparently the action is reduction of the nitro group.

As a check upon this view, 2 g. of nitrobenzene is dissolved in ether, the calculated quantity of phenylarsine added and the solution sealed in a flask filled with carbon dioxide. After standing overnight, it is found that the nitrobenzene is reduced to hydrazobenzene, m. p. 128–132°.



**Cinnamic Aldehyde** reacts vigorously when mixed with an equimolecular proportion of phenylarsine. Even in the presence of conc. hydrochloric acid, reduction takes place. The reaction mixture is extracted with ether, the arsenobenzene filtered off, the ethereal solution evaporated, and the residual oil identified as cinnamic alcohol by preparation of the phenylurethane<sup>28</sup> derivative, m. p. 90–92°.

**Crotonic Aldehyde** and **Salicylic Aldehyde** are reduced in a similar manner with the formation of arsenobenzene and other products which have not been identified.

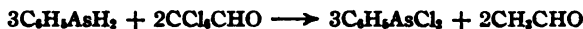
<sup>26</sup> Ber., 19, 2376 (1886).

<sup>27</sup> Am. Chem. J., 2, 88 (1880).

<sup>28</sup> Rosenthaler, "Der Nachweis organischer Verbindungen," Ferdinand Enke, Stuttgart, 1914, p. 87.

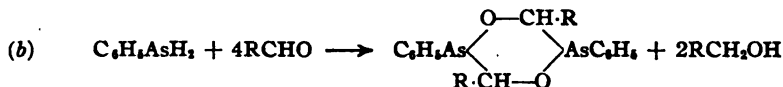
**Chloral.**—When chloral or chloral hydrate is allowed to react with phenylarsine according to the general method for the preparation of *bis*-( $\alpha$ -hydroxyalkyl)arylsarsines, a violent reaction takes place. On distillation of the reaction mixture much excess of chloral is recovered. The fraction which boils at 180–182° at 70 mm. consists of phenylarsenious chloride.

In another experiment, 3.5 g. of chloral is placed in a Claisen flask filled with carbon dioxide connected to a glass worm surrounded by a freezing mixture. Five g. of phenylarsine is added drop by drop through a separatory funnel. A considerable quantity of gas is lost, but the few drops of distillate collected in a well-cooled receiver are identified as acetaldehyde by boiling point and aldehyde test. Some arsenobenzene is obtained despite rigid exclusion of air. Doubtless this is formed by interaction<sup>29</sup> of  $C_6H_5AsCl_2$  and  $C_6H_5AsH_2$ .



### Summary

1. Primary aryl arsines and aldehydes react in three ways, depending upon the conditions of the reaction, as shown by the following equations.



2. Aromatic primary arsines and aliphatic aldehydes condense in the presence of conc. hydrochloric acid at room temperature to give compounds of the formula  $C_6H_5As(CHOHR)_2$ .

3. Aromatic primary arsines condense with aromatic aldehydes, with or without a solvent, best in the presence of hydrogen chloride to give compounds of the general formula  $C_6H_5As(CHOHR)_2$ .

4. Primary aromatic arsines condense with aliphatic aldehydes in the presence of anhydrous hydrochloric acid to give tetrahydro-dioxdiarsines of the general formula given in (1b). These same substances may be formed by the action of acetyl chloride, acetic anhydride, or anhydrous hydrochloric acid upon compounds mentioned in (2).

5a. The substances  $RA_s(CHOHR)_2$ , where the aldehyde used is aliphatic, oxidize readily in the air to form an arylarsonic acid and aldehyde. Other oxidizing agents, such as potassium permanganate or nitric acid, cause decomposition to take place in the same way. Air does not oxidize most of the compounds which are derived from aromatic aldehydes.

<sup>29</sup> Ger. pat., 254,187, Ber., 46, 3565 (1913).

5b. With halogens, phosphorus pentachloride and phenylarsenious chloride, products are obtained which would be expected, providing the original substances were mechanical mixtures of aldehyde and arsine. The compounds may be titrated quantitatively with a solution of iodine in ether.

5c. The compounds form unstable addition products with halogen acids, and stable addition compounds with chloroplatinic acid.

6a. The tetrahydro-dioxdiarsines formed according to Equation (1b), oxidize in the air to give aryl arsine oxides and aldehydes. This is particularly noticeable where the product is a derivative of formaldehyde.

6b. The compounds form double salts with chloroplatinic acid and cupric chloride.

6c. With iodine or phosphorus pentachloride, products are obtained which might be expected from a mixture of aryl arsine and aldehyde.

7. Aromatic primary arsines reduce aromatic aldehydes to alcohols with the formation of arsenobenzene, when a mixture is made at room temperature with no hydrochloric acid as a catalyst, or when a mixture is heated with or without hydrochloric acid.

8. A discussion of the structure of the various condensation products is given.

9. The probable mechanism for the condensation of aromatic primary arsines and aromatic arsine oxides, antimony tri-chloride, etc., is discussed.

URBANA, ILLINOIS

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

## AN ELECTROCHEMICAL STUDY OF THE REVERSIBLE REDUCTION OF ORGANIC COMPOUNDS<sup>1</sup>

BY J. B. CONANT, H. M. KAHN, L. F. FIESER AND S. S. KURTZ, JR.

Received April 6, 1922

### Introduction

Certain organic substances, such as anthraquinone, indigo and the vat dyes, have the rather unique property of being easily reduced in aqueous solutions by such reagents as sodium hydrosulfite and titanous chloride. The reaction is readily reversible, and the reduced material may be re-oxidized by almost any mild oxidizing agent, and even by oxygen itself. These reactions are very rapid, and take place at room temperature. They seem to involve a different kind of process from such irreversible reductions as the hydrogenation of ethylene derivatives, or the reduction of aldehydes, ketones, and nitriles. It is of interest to determine, if possible, the mecha-

<sup>1</sup> The theoretical portions of this paper and an account of some preliminary experiments were presented to the Northeastern Section of the American Chemical Society, April 8, 1921.

nism of each of these two classes of reduction reactions and to discover what particular type of compound is essential for each.

The experiments described in this preliminary paper deal with the oxidation-reduction potentials of certain water-soluble substances related to the vat dyes, namely the salts of six anthraquinone sulfonic acids. The results show that the reduction of these substances is strictly reversible, and the oxidation-reduction potential may be readily measured. These reactions are, therefore, in every way comparable with such inorganic processes as the reduction of ferric salts. Such reactions appear to involve only the gain or loss of one or more electrons; the application of the principles of electrochemistry, therefore, seems justified, and leads to some interesting generalizations. On the other hand, many of the more usual cases of the reduction of organic substances do not seem to involve merely electron transfer. In the reduction of ethylene and its derivatives, for example, hydrogen atoms are actually added to the molecule; the reaction is not reversible. Such reductions are brought about not by reagents like hydrosulfite or titanous chloride, but by hydrogen and a catalyst, or by some metal capable of liberating "nascent" hydrogen. The conception of oxidation-reduction potentials does not seem applicable to such irreversible hydrogenations.

The conjugated system,  $O=C-C=C-C=O$ , is characteristic of many substances which undergo reversible reduction. The simplest case is that of quinone. Indigo and the indigoids, as well as anthraquinone and some of the vat dyes derived from it all contain this system. Haber and Russ<sup>2</sup> have carefully measured the potential of the system quinone-hydroquinone in acid solution. Recently Granger and Nelson<sup>3</sup> have repeated Haber's work. Clark<sup>4</sup> has studied the oxidation-reduction potential of indigo carmine and certain other dyestuffs and obtained reproducible and consistent results. All these investigations have shown that the reduction of certain organic compounds in acid solution can be expressed in terms of the general principles of electrochemistry.

In acid solution, the reaction may be represented thus: (A = oxidized form,  $AH_2$  = reduced)



The potential of such a reaction is expressed by the well-known formula

$$\pi = \pi_0 + 0.059 \log [H^+] + 0.0295 \log [A]/[AH_2] \quad (1)$$

where [A] is the concentration of oxidized form, and  $[AH_2]$  is the concentration of the reduced form.

$$\pi = \pi_0, \text{ obviously, when } [H^+] = 1, \text{ and } [A]/[AH_2] = 1$$

<sup>2</sup> Haber and Russ, *Z. physik. Chem.*, **47**, 257 (1904).

<sup>3</sup> Granger and Nelson, *THIS JOURNAL*, **43**, 1401 (1921).

<sup>4</sup> Clark, *J. Wash. Acad. Sci.*, **10**, 255 (1920); *Science*, **54**, 557 (1921).



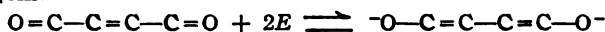
This formula was shown by Haber and Russ to express accurately all their experimental results with quinone.

While the system quinone:hydroquinone is reversible in acid solution, side reactions make it essentially irreversible in alkaline solutions, and no constant values could be obtained by Granger and Nelson. The reactions at present under investigation are reversible in both acid and alkaline solutions. Therefore, for the first time, it has been possible to measure the potential of an organic reduction process over a wide range of hydrogen-ion concentration.

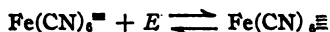
A consideration of the reaction in alkaline solution (the most usual condition for vat dye reduction) leads to a slightly different point of view from that represented in Equation 1. The reduction product,  $AH_2$ , is an acid, and in alkaline solution is very largely present in the form of the ion  $A^{--}$ . The reduction, therefore, under these conditions is practically



Only the transfer of two electrons is involved. If the structure of the substances under investigation is examined, it will be observed that this process of reduction is essentially a 1,6 addition of two electrons to a conjugated system.



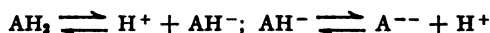
This reaction is in form exactly like those for such inorganic processes as



Considering the reaction from this point of view the equation for the single oxidation-reduction electrode at 25° would be

$$\pi = \pi'_0 + 0.0295 \log ([A]/[A^{--}]) \quad (2)$$

The reduced material is a weak dibasic acid, and dissociates according to the following equations.



The concentration of the divalent ion  $A^{--}$  can, therefore, be expressed in terms of the total concentration of the reduced material,  $([AH_2]_T)$ , (which is what is really measured) in accordance with the following considerations.

$$K_1 = \frac{[H^+][AH^-]}{[AH_2]}; K_2 = \frac{[H^+][A^{--}]}{[AH^-]}$$

$$[AH_2]_T = [A^{--}] + [AH^-] + [AH_2]$$

From this it follows that

$$[A^{--}] = K_1 K_2 [AH_2]_T / (K_1 K_2 + [H^+]^2 + K_1 [H^+])$$

Substituting this value in Equation 2 we have

$$\pi = \pi'_0 + 0.0295 \log ([A]/[AH_2]_T) - 0.0295 \log K_1 K_2 \\ + 0.0295 \log (K_1 K_2 + [H^+]^2 + K_1 [H^+])$$

The last term can be expressed more conveniently by multiplying and dividing by  $[H^+]^2$  which gives:

$$\pi = \pi'_0 + 0.0295 \log ([A]/[AH_2]_T) - 0.0295 \log K_1 K_2 + 0.059 \log [H^+] + 0.0295 \log \{K_1(K_2 + [H^+]/[H^+]^2) + 1\} \quad (3)$$

Equation 3 is thus a general expression for the oxidation-reduction potential in both acid and alkaline solutions. Since the reduced compounds are very weak acids, Equation 3 can be simplified when applied to the potentials measured in acid solutions. The last term is, under these conditions, negligible and  $[AH_2] = [AH_2]_T$ , therefore

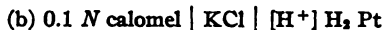
$$\pi = \pi'_0 + 0.0295 \log ([A]/[AH_2]) - 0.0295 \log K_1 K_2 + 0.059 \log [H^+]$$

Comparing this modified Equation 3 with Equation 1, which also expresses the potential in acid solution, we see that

$$\pi_0 = \pi'_0 - 0.0295 \log K_1 K_2. \quad (4)$$

This relationship is obviously correct since  $\pi_0$  is a measure of the free energy of the formation of  $AH_2$  from  $A$ ,  $\pi'_0$  a measure of the free energy of formation of  $A^{--}$  from  $A$ , and  $0.0295 \log K_1 K_2$  corresponds to the free energy change in the dissociation of  $AH_2$  into  $A^{--}$ .

In order to test the applicability of Equation 3 the electromotive force of the following two types of cells was measured.



The mixture of oxidized and reduced material was obtained by adding definite increments of a reducing agent to a solution of the oxidized form. The hydrogen-ion concentration was controlled by means of "buffer" solutions. The observed value of the potential of the hydrogen electrode (Cell b) supplied the necessary information in regard to the hydrogen-ion concentration; the potential of Cell a was the required oxidation-reduction potential, and a knowledge of the amount of reducing agent added enabled one to calculate the value for the ratio of  $[A]/[AH_2]_T$ .<sup>5</sup> As will be shown below, the results thus obtained were in accord with Equation 3.

### Apparatus and Materials

The oxidation-reduction potentials were measured on 2 platinum electrodes (one bright, the other platinized) immersed in the solution which was contained in a glass cell of 400 cc. capacity. The contents of the cell were agitated by a glass stirrer working through a mercury seal and driven by an electric motor by means of a flexible shaft. An agar-agar bridge saturated with potassium chloride made connection with a 0.1 *N* calomel electrode. The cell could be swept free from air by the introduction of nitrogen free from oxygen. The reducing agent was contained in a buret the tip of which was fitted to a tube leading to the bottom of the cell; this served also as the inlet tube for the nitrogen.

It was found convenient to have the cell also equipped with a hydrogen

<sup>5</sup> Clark first used this method in his studies (Ref. 4); his paper, however, did not come to our attention until after we had developed a similar procedure.

electrode of the Hildebrand type through which hydrogen was bubbled when desired. By this arrangement the potential of the hydrogen electrode was determined in the same apparatus as the oxidation-reduction potential. As will be evident later, any errors due to liquid junctions or to the calomel cell were thus canceled in the final calculations.

The electromotive force was measured on a Leeds and Northrup student potentiometer accurate to about 0.5 mv. The temperature of the cells was kept at 25° within a degree.

The organic compounds used in this work were the salts of 6 anthraquinone sulfonic acids.<sup>6</sup> As shown by the titration curves, they contained considerable amounts of inert material which, however, did not interfere with the determination of the oxidation-reduction potentials by the present method. It might be noted that two samples of the  $\beta$  salt from different laboratories yielded identical results. The purities of the sodium salts of the  $\alpha$ -,  $\beta$ -, the 2,6-, the 2,7- and the 1,5-sulfonic acids were 96, 95, 94, 87 and 92%, respectively. The 1,5- and the 1,8-calcium salts were 83 and 56% pure, respectively. Two reducing agents were employed; titanous chloride in 0.1 *N* acid solutions, and sodium hydrosulfite in all other solutions. Difficulties were encountered with titanous chloride in both citrate and acetate buffer solutions in the range of Sørensen value  $P_H$  2 to  $P_H$  7, complex precipitates being formed. Hydrosulfite is decomposed by even dil. acids, but it was found that it could be used in acid solutions because the speed of its oxidation by the anthraquinone derivative is much greater than that of its decomposition by the acid.

### Control of the Hydrogen-ion Concentration

The concentration of the hydrogen ion could not be determined in the presence of the anthraquinone derivative. It was thus necessary to keep the hydrogen ion at a constant value by means of a buffer solution during the addition of the reducing agent. Except in 0.1 *N* acid and alkali, buffer solutions such as those described by Clark<sup>7</sup> were employed. Since the concentration of organic substance was very low (0.003 *M*) it seemed that such buffer solutions would keep the hydrogen-ion concentration constant throughout the reduction. The solutions were not made up determinate but were adjusted to the desired hydrogen-ion concentration which was determined by the hydrogen electrode just before the anthraquinone derivative was added. For the range  $P_H$  10 to 12, a sodium phenolate solution was used with good results. It was not stable, however, for longer than a day.

Certain of the compounds investigated are rapidly decomposed by solu-

<sup>6</sup> With one exception kindly furnished by E. I. Du Pont de Nemours and Company.

<sup>7</sup> "The Determination of Hydrogen Ions," by W. M. Clark, Williams and Wilkins, 1920.

tions of sodium hydroxide 0.1 *N* or stronger. In citrate buffer solutions of the same hydrogen-ion concentration, however, the substances are stable. The use of buffer solutions, therefore, enabled us to measure the potentials of these compounds in the range  $P_H$  11 to 13.

### Procedure

The buffer solution (350 cc.) was introduced into the cell and the potential of the hydrogen electrode determined. One thousandth of a mole of the anthraquinone sulfonic acid in the form of its sodium or calcium salt was then added. The cell was swept free from air, the stirrer started and the reducing agent added in suitable increments from a buret. Fresh solutions of the hydrosulfite (1.25 g. in 100 cc.) were prepared for each run; the titanous chloride was also diluted to a 1% solution just before the beginning of the run in which it was to be used. The solution in the buret was protected by a layer of benzene.

After the addition of each increment of reducing agent, the potentials of both the bright and platinized electrodes were determined. No more reducing agent was added until both electrodes came to the same value which was then recorded. In a few cases (at about  $P_H$  3), the potential of the platinized electrode gave consistent and reproducible values which were considered correct, although the bright electrode gave lower and variable potentials. The electrodes soon came to equilibrium when the solutions were rapidly stirred; without stirring it would be necessary to wait about 30 min. after the addition of each increment. The course of the

reduction was followed by plotting the potential against the increments of reducing agent. Fig. 1 shows some typical titration curves thus obtained (the variations in the slope are discussed below). By an inspection of these curves it is possible to determine the end-point of the titration with considerable accuracy. Taking this value as 100% reduction, the increments of the reducing agent may now be expressed in terms of percentage

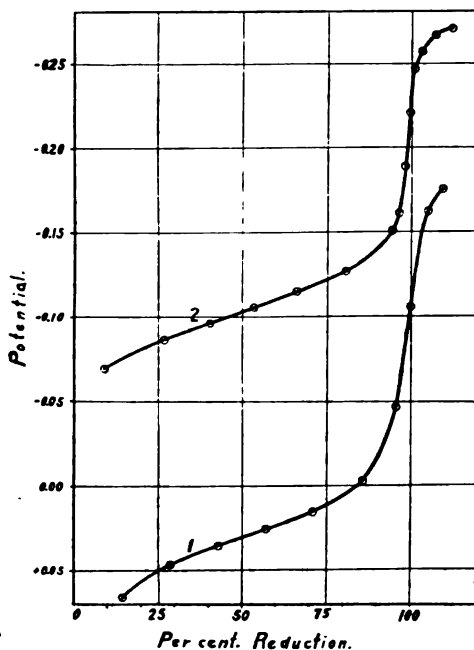


Fig. 1.—Typical titration curves.

Curve 1: disodium salt of anthraquinone-2,7-disulfonic acid;  $P_H$  3.44. Curve 2: sodium salt of anthraquinone- $\beta$ -sulfonic acid  $P_H$  3.83.

reduction as in Fig. 1. The value for the potential at the mid-point (50% reduction) can now be determined by graphical interpolation of the curve.

Such a procedure as the one just outlined might be found useful for determining the purity of anthraquinone derivatives and similar compounds. The details of such an analytical method have not yet been elaborated.

### Experimental Results

Table I summarizes the results obtained in this investigation. All the electromotive force measurements are given as single potentials in *volts referred to the normal hydrogen electrode as zero*. Thus the values for the hydrogen electrode ( $\pi_h$ ) and the oxidation-reduction electrode at the

TABLE I  
SODIUM SALT OF ANTHRAQUINONE BETA SULFONIC ACID

Hydrogen-ion conc. [H <sup>+</sup> ]	Hydrogen electrode $\pi_h$ v.	Oxidation-reduction electrode $\Delta\pi_1$ ( $m=0.2$ ) v.	$\Delta\pi_2$ ( $m=0.8$ ) v.	$\pi_h - \pi_o$ v.	$\pi_h - \pi_h$ v.	Calc. dissociation constants	Nature of buffer solution
$6.03 \times 10^{-2}$	-0.072	+0.117	0.023	0.024	0.189	....	HCl
$4.07 \times 10^{-2}$	-0.082	+0.105	0.023	0.024	0.187	....	KCl + HCl
$1.41 \times 10^{-1}$	-0.227	-0.035	0.031	0.023	0.192	....	NaAc + HAc
$1.86 \times 10^{-2}$	-0.279	-0.096	0.024	0.027	0.183	....	NaAc + HAc
$5.79 \times 10^{-3}$	-0.309	-0.129	0.022	0.023	0.180	....	NaAc + HAc
$1.41 \times 10^{-3}$	-0.345	-0.154	0.024	0.025	0.191	....	NaAc + HAc
$6.52 \times 10^{-4}$	-0.365	-0.176	0.020	0.022	0.189	....	KH <sub>2</sub> PO <sub>4</sub> + NaOH
$1.86 \times 10^{-4}$	-0.397	-0.214	0.022	0.020	0.183	....	KH <sub>2</sub> PO <sub>4</sub> + NaOH
$1.26 \times 10^{-4}$	-0.407	-0.223	0.024	0.022	0.184	....	KH <sub>2</sub> PO <sub>4</sub> + NaOH
$8.55 \times 10^{-5}$	-0.417	-0.232	0.021	0.023	0.185	....	KH <sub>2</sub> PO <sub>4</sub> + NaOH
$2.27 \times 10^{-5}$	-0.451	-0.258	0.019	0.020	0.193	....	KH <sub>2</sub> PO <sub>4</sub> + NaOH
				Av.	0.187	....	
$7.31 \times 10^{-3}$	-0.480	-0.277	0.015	0.018	...	0.016	$2 \times 10^{-3}$ KH <sub>2</sub> PO <sub>4</sub> + NaOH
$6.03 \times 10^{-3}$	-0.485	-0.278	0.014	0.017	...	0.020	$2 \times 10^{-3}$ KH <sub>2</sub> PO <sub>4</sub> + NaOH
$2.45 \times 10^{-3}$	-0.508	-0.304	0.025	0.019	...	0.017	$0.7 \times 10^{-3}$ Borax + H <sub>2</sub> BO <sub>3</sub>
$1.41 \times 10^{-3}$	-0.522	-0.319	0.023	0.017	...	0.016	$0.4 \times 10^{-3}$ Borax + H <sub>2</sub> BO <sub>3</sub>
$6.26 \times 10^{-4}$	-0.543	-0.323	0.018	0.015	...	0.033	$0.8 \times 10^{-3}$ H <sub>2</sub> BO <sub>3</sub> + NaOH
$2.45 \times 10^{-4}$	-0.567	-0.335	0.014	0.017	...	0.045	$0.8 \times 10^{-3}$ H <sub>2</sub> BO <sub>3</sub> + NaOH
$7.59 \times 10^{-5}$	-0.597	-0.350	0.014	0.014	...	0.060	$0.7 \times 10^{-3}$ H <sub>2</sub> BO <sub>3</sub> + NaOH
$2.45 \times 10^{-5}$	-0.626	-0.370	0.037	0.023	...	0.069	$0.3 \times 10^{-3}$ Phenol + NaOH
$7.03 \times 10^{-5}$	-0.658	-0.383	0.034	0.022	...	0.088	$5 \times 10^{-3}$ Phenol + NaOH
$1.38 \times 10^{-3}$	-0.700	-0.381	0.044	0.025	...	0.132	$5 \times 10^{-3}$ Phenol + NaOH
$1.38 \times 10^{-3}$	-0.700	-0.380	0.028	0.018	...	0.133	$6 \times 10^{-3}$ Glycocoll + NaOH
$6.27 \times 10^{-3}$	-0.720	-0.381	0.058	0.014	...	0.152	$5 \times 10^{-3}$ Citrate + NaOH
$1.88 \times 10^{-3}$	-0.751	-0.384	0.039	0.033	...	0.180	$4 \times 10^{-3}$ Citrate + NaOH
$1.55 \times 10^{-3}$	-0.756	-0.379	0.034	0.032	...	0.190	$7 \times 10^{-3}$ Glycocoll + NaOH
$8.89 \times 10^{-4}$	-0.770	-0.393	0.027	0.034	...	0.190	$2 \times 10^{-3}$ KOH
				Av. (first eight),	$K_1 = 1 \times 10^{-3}$		
				Av. (last seven),	$K_1 K_2 = 5 \times 10^{-10}$		
DISODIUM SALT OF ANTHRAQUINONE-2,6-DISULFONIC ACID							
$3.63 \times 10^{-3}$	-0.085	+0.143	0.023	0.033	0.228	....	HCl
$1.41 \times 10^{-1}$	-0.227	+0.001	0.030	0.031	0.228	....	NaAc + HAc
$1.41 \times 10^{-2}$	-0.345	-0.120	0.024	0.033	0.225	....	NaAc + HAc
$1.26 \times 10^{-4}$	-0.407	-0.181	0.024	0.032	0.226	....	KH <sub>2</sub> PO <sub>4</sub> + NaOH
$2.27 \times 10^{-5}$	-0.451	-0.220	0.019	0.027	0.231	....	KH <sub>2</sub> PO <sub>4</sub> + NaOH
				Av.	0.228	....	
$9.62 \times 10^{-3}$	-0.532	-0.275	0.024	0.032	...	0.029	$0.8 \times 10^{-3}$ Borax + H <sub>2</sub> BO <sub>3</sub>
$2.36 \times 10^{-3}$	-0.568	-0.292	0.021	0.027	...	0.048	$0.9 \times 10^{-3}$ H <sub>2</sub> BO <sub>3</sub> + NaOH

$3.24 \times 10^{-11}$	-0.619	-0.311	0.040	0.036	...	0.080	$1 \times 10^{-10}$	Phenol + NaOH
$7.91 \times 10^{-12}$	-0.655	-0.321	0.042	0.041	...	0.106	$0.6 \times 10^{-10}$	Phenol + NaOH
$5.37 \times 10^{-12}$	-0.665	-0.324	0.035	0.035	...	0.113	$2 \times 10^{-10}$	Phenol + NaOH
$1.32 \times 10^{-12}$	-0.701	-0.326	0.038	0.040	...	0.147	$2 \times 10^{-10}$	Phenol + NaOH
$6.26 \times 10^{-13}$	-0.720	-0.326	0.043	0.042	...	0.166	$2 \times 10^{-10}$	Citrate + NaOH
$8.89 \times 10^{-14}$	-0.770	-0.325	0.037	0.046	...	0.217	$2 \times 10^{-10}$	KOH

 Av. (first four)  $K_1 = 8 \times 10^{-7}$ 

 Av. (last four)  $K_1 K_2 = 2 \times 10^{-10}$ 

## DICALCIUM SALT OF ANTHRAQUINONE-1,8-DISULFONIC ACID

$7.32 \times 10^{-3}$	-0.067	+0.135	0.035	0.024	0.202	...	.....	HCl
$7.59 \times 10^{-4}$	-0.184	+0.012	0.045	0.026	0.196	...	.....	Citrate + HCl
$1.17 \times 10^{-4}$	-0.232	-0.035	0.045	0.026	0.197	...	.....	NaAc + HAc
$1.86 \times 10^{-5}$	-0.279	-0.069	0.022	0.030	0.210	...	.....	NaAc + HAc
$1.05 \times 10^{-5}$	-0.353	-0.144	0.047	0.027	0.209	...	.....	$\text{KH}_2\text{PO}_4$ + NaOH
$8.55 \times 10^{-6}$	-0.417	-0.206	0.044	0.027	0.211	...	.....	$\text{KH}_2\text{PO}_4$ + NaOH
$1.26 \times 10^{-6}$	-0.466	-0.252	0.045	0.030	0.214	...	.....	$\text{KH}_2\text{PO}_4$ + NaOH

Av. 0.206

$6.76 \times 10^{-10}$	-0.541	-0.303	0.038	0.037	...	0.032	$0.7 \times 10^{-10}$	Borax + $\text{H}_2\text{BO}_3$
$8.89 \times 10^{-11}$	-0.593	-0.332	0.034	0.025	...	0.055	$0.7 \times 10^{-10}$	$\text{H}_2\text{BO}_3$ + NaOH
$1.17 \times 10^{-11}$	-0.645	-0.351	0.050	0.033	...	0.088	$1 \times 10^{-10}$	Phenol + NaOH
$3.63 \times 10^{-12}$	-0.675	-0.371	0.040	0.030	...	0.098	$0.7 \times 10^{-10}$	Phenol + NaOH
$1.23 \times 10^{-12}$	-0.703	-0.383	0.043	0.041	...	0.114	$0.7 \times 10^{-10}$	Phenol + NaOH
$4.58 \times 10^{-13}$	-0.728	-0.405	0.042	0.039	...	0.117	$0.4 \times 10^{-10}$	Phenol + NaOH
$4.25 \times 10^{-13}$	-0.730	-0.407	0.040	0.032	...	0.117	$0.4 \times 10^{-10}$	Citrate + NaOH
$3.22 \times 10^{-13}$	-0.737	-0.419	0.040	0.036	...	0.112	$0.2 \times 10^{-10}$	Citrate + NaOH
$1.87 \times 10^{-13}$	-0.751	-0.413	0.046	0.036	...	0.132	$0.6 \times 10^{-10}$	Citrate + NaOH
$4.77 \times 10^{-14}$	-0.786	-0.413	0.049	0.035	...	0.167	$2 \times 10^{-10}$	KOH

 Av.  $K_1 = 7 \times 10^{-7}$ 
 $K_1 K_2$  is negligible

## DISODIUM SALT OF ANTHRAQUINONE-2,7-DISULFONIC ACID

$3.63 \times 10^{-3}$	-0.085	+0.132	0.025	0.025	0.217	...	.....	HCl
$2.55 \times 10^{-3}$	-0.153	+0.070	0.024	0.025	0.223	...	.....	Citrate + HCl
$1.41 \times 10^{-4}$	-0.227	+0.005	0.025	0.026	0.232	...	.....	NaAc + HAc
$1.95 \times 10^{-5}$	-0.278	-0.049	0.021	0.025	0.229	...	.....	NaAc + HAc
$3.63 \times 10^{-6}$	-0.321	-0.092	0.026	0.026	0.229	...	.....	NaAc + HAc
$1.86 \times 10^{-7}$	-0.397	-0.167	0.023	0.020	0.230	...	.....	$\text{KH}_2\text{PO}_4$ + NaOH
$2.27 \times 10^{-8}$	-0.451	-0.205	0.021	0.024	0.246	...	.....	$\text{KH}_2\text{PO}_4$ + NaOH

Av. 0.229

$1.32 \times 10^{-9}$	-0.524	-0.268	0.013	0.016	...	0.027	$1 \times 10^{-10}$	Borax + $\text{H}_2\text{BO}_3$
$9.62 \times 10^{-10}$	-0.532	-0.263	0.028	0.024	...	0.040	$2 \times 10^{-10}$	Borax + $\text{H}_2\text{BO}_3$
$4.57 \times 10^{-10}$	-0.551	-0.274	0.021	0.027	...	0.048	$2 \times 10^{-10}$	$\text{H}_2\text{BO}_3$ + NaOH
$2.36 \times 10^{-10}$	-0.568	-0.278	0.023	0.019	...	0.061	$3 \times 10^{-10}$	$\text{H}_2\text{BO}_3$ + NaOH
$7.03 \times 10^{-11}$	-0.599	-0.292	0.025	0.028	...	0.078	$3 \times 10^{-10}$	Glycocoll + NaOH
$1.58 \times 10^{-11}$	-0.637	-0.312	0.031	0.031	...	0.096	$5 \times 10^{-10}$	Phenol + NaOH
$1.17 \times 10^{-11}$	-0.645	-0.311	0.034	0.035	...	0.105	$5 \times 10^{-10}$	Phenol + NaOH
$7.91 \times 10^{-12}$	-0.655	-0.319	0.036	0.036	...	0.107	$3 \times 10^{-10}$	Phenol + NaOH
$1.38 \times 10^{-12}$	-0.700	-0.319	0.032	0.031	...	0.152	$3 \times 10^{-10}$	Phenol + NaOH
$1.38 \times 10^{-13}$	-0.700	-0.314	0.030	0.030	...	0.157	$4 \times 10^{-10}$	Glycocoll + NaOH
$4.25 \times 10^{-13}$	-0.730	-0.311	0.028	0.032	...	0.190	$5 \times 10^{-10}$	Citrate + NaOH
$3.35 \times 10^{-13}$	-0.736	-0.315	0.037	0.046	...	0.192	$4 \times 10^{-10}$	Citrate + NaOH
$1.95 \times 10^{-13}$	-0.750	-0.319	0.046	0.043	...	0.202	$3 \times 10^{-10}$	KOH
$2.02 \times 10^{-14}$	-0.808	-0.298	0.040	0.044	...	0.281	$1 \times 10^{-10}$	KOH

 Av. (first five),  $K_1 = 2 \times 10^{-7}$ 

 Av. (last nine),  $K_1 K_2 = 5 \times 10^{-10}$ 

## POTASSIUM SALT OF ANTHRAQUINONE ALPHA SULFONIC ACID

$1.66 \times 10^{-1}$	-0.046	+0.150	0.020	0.020	0.196	...	.....	HCl
$7.93 \times 10^{-3}$	-0.065	+0.134	0.020	0.019	0.199	...	.....	HCl
$4.07 \times 10^{-4}$	-0.200	-0.007	0.022	0.021	0.193	...	.....	NaAc + HAc
$7.03 \times 10^{-5}$	-0.245	-0.066	0.023	0.018	0.189	...	.....	Citrate + HCl
$5.36 \times 10^{-6}$	-0.311	-0.111	0.025	0.019	0.200	...	.....	NaAc + HAc
$2.19 \times 10^{-7}$	-0.334	-0.136	0.027	0.022	0.198	...	.....	Citrate + NaOH
$1.95 \times 10^{-8}$	-0.396	-0.210	0.020	0.018	0.186	...	.....	$\text{KH}_2\text{PO}_4$ + NaOH
$2.55 \times 10^{-9}$	-0.448	-0.247	0.018	0.016	0.201	...	.....	Borax + $\text{H}_2\text{BO}_3$

Av. 0.195

TABLE I (continued)

Hydrogen-ion conc. [H <sup>+</sup> ]	Hydrogen electrode $\pi_h$ v.	Oxidation-reduction electrode $\pi_n$ v.	$\Delta\pi_1$ ( $m=0.2$ ) v.	$\Delta\pi_2$ ( $m=0.8$ ) v.	$\pi_n - \pi_h$ $=\pi_o$ v.	$\pi_n - \pi_h$ $=\pi_o$ v.	Calc. dissociation constants	Nature of buffer solution
$1.36 \times 10^{-9}$	-0.523	-0.311	0.019	0.017	...	0.017	$3 \times 10^{-9}$	Borax + H <sub>2</sub> BO <sub>3</sub>
$9.25 \times 10^{-11}$	-0.592	-0.355	0.018	0.018	...	0.042	$2 \times 10^{-9}$	Phenol + NaOH
$4.76 \times 10^{-11}$	-0.609	-0.364	0.018	0.014	...	0.050	$2 \times 10^{-9}$	Phenol + NaOH
$4.41 \times 10^{-12}$	-0.670	-0.387	0.016	0.013	...	0.088	$3 \times 10^{-9}$	Phenol + NaOH
$2.45 \times 10^{-12}$	-0.685	-0.395	0.013	0.014	...	0.095	$4 \times 10^{-9}$	Phenol + NaOH
$4.99 \times 10^{-12}$	-0.726	-0.414	0.020	0.019	...	0.117	$5 \times 10^{-9}$	Citrate + NaOH
$3.89 \times 10^{-12}$	-0.732	-0.420	0.015	0.015	...	0.117	$4 \times 10^{-9}$	Phenol + NaOH
$2.63 \times 10^{-12}$	-0.742	-0.423	0.019	0.020	...	0.124	$4 \times 10^{-9}$	Citrate + NaOH
$8.59 \times 10^{-14}$	-0.771	-0.436	0.021	0.019	...	0.130	$5 \times 10^{-9}$	Citrate + NaOH
$5.67 \times 10^{-14}$	-0.782	-0.444	0.022	0.020	...	0.143	$4 \times 10^{-9}$	Citrate + NaOH
Av. $K_1 = 4 \times 10^{-9}$ $K_1K_2$ is negligible								
DISODIUM SALT OF ANTHRAQUINONE-1,5-DISULFONIC ACID								
$2.36 \times 10^{-11}$	-0.037	+0.199	0.017	0.019	0.236	...	.....	HCl
$9.61 \times 10^{-12}$	-0.060	+0.176	0.018	0.019	0.236	...	.....	HCl
$3.77 \times 10^{-12}$	-0.084	+0.154	0.017	0.018	0.238	...	.....	HCl
$1.37 \times 10^{-12}$	-0.228	+0.011	0.022	0.023	0.239	...	.....	NaAc + HAc
$3.63 \times 10^{-12}$	-0.321	-0.081	0.024	0.025	0.240	...	.....	NaAc + HAc
$5.57 \times 10^{-12}$	-0.428	-0.191	0.036	0.028	0.237	...	.....	NaAc + HAc
$9.62 \times 10^{-12}$	-0.532	-0.290	0.018	0.019	0.242	...	.....	KH <sub>2</sub> PO <sub>4</sub> + NaOH
$4.57 \times 10^{-12}$	-0.551	-0.307	...	0.019	0.243	...	.....	H <sub>2</sub> BO <sub>3</sub> + NaOH
$4.24 \times 10^{-11}$	-0.612	-0.372	0.017	0.016	0.240	...	.....	Phenol + NaOH
$3.35 \times 10^{-11}$	-0.618	-0.379	0.015	0.016	0.239	...	.....	Phenol + NaOH
Av. $K_1 = 0.239$								
$3.92 \times 10^{-12}$	-0.673	-0.422	0.015	0.016	...	0.012	$4 \times 10^{-12}$	Phenol + NaOH
$9.60 \times 10^{-12}$	-0.709	-0.454	0.013	0.014	...	0.016	$2 \times 10^{-12}$	Phenol + NaOH
$4.58 \times 10^{-12}$	-0.728	-0.468	0.019	0.018	...	0.021	$2 \times 10^{-12}$	Glycocoll + NaOH
$1.87 \times 10^{-12}$	-0.751	-0.485	0.022	0.021	...	0.027	$2 \times 10^{-12}$	Glycocoll + NaOH
$1.73 \times 10^{-12}$	-0.753	-0.494	0.029	0.020	...	0.020	$0.6 \times 10^{-12}$	NaOH
$1.26 \times 10^{-12}$	-0.761	-0.489	0.025	0.022	...	0.033	$2 \times 10^{-12}$	Citrate + NaOH
$8.89 \times 10^{-14}$	-0.770	-0.499	0.025	0.022	...	0.032	$1 \times 10^{-12}$	KOH
$3.77 \times 10^{-14}$	-0.792	-0.498	0.033	0.031	...	0.055	$4 \times 10^{-12}$	NaOH
$3.35 \times 10^{-14}$	-0.795	-0.502	0.035	0.028	...	0.054	$2 \times 10^{-12}$	NaOH
$2.75 \times 10^{-14}$	-0.800	-0.500	0.040	0.031	...	0.061	$3 \times 10^{-12}$	NaOH
Av. $K_1 = 3 \times 10^{-12}$ $K_1K_2$ is negligible								
DICALCIUM SALT OF ANTHRAQUINONE-1,5-DISULFONIC ACID								
$2.36 \times 10^{-11}$	-0.037	+0.199	0.020	0.018	0.236	...	.....	HCl
$9.61 \times 10^{-12}$	-0.060	+0.178	0.020	0.022	0.238	...	.....	HCl
$1.12 \times 10^{-12}$	-0.233	+0.002	0.029	0.024	0.235	...	.....	NaAc + HAc
$4.96 \times 10^{-12}$	-0.318	-0.080	0.020	0.022	0.233	...	.....	NaAc + HAc
$1.05 \times 10^{-12}$	-0.412	-0.175	0.020	0.024	0.237	...	.....	KH <sub>2</sub> PO <sub>4</sub> + NaOH
$3.48 \times 10^{-12}$	-0.558	-0.313	0.020	0.019	0.245	...	.....	Phenol + NaOH
$3.35 \times 10^{-11}$	-0.618	-0.374	0.027	0.020	0.244	...	.....	Phenol + NaOH
Av. $K_1 = 0.238$								
$4.58 \times 10^{-12}$	-0.669	-0.407	0.028	0.026	...	0.024	$3 \times 10^{-11}$	Phenol + NaOH
$1.41 \times 10^{-12}$	-0.699	-0.433	0.034	0.019	...	0.028	$1 \times 10^{-11}$	Phenol + NaOH
$2.09 \times 10^{-12}$	-0.748	-0.475	0.043	0.024	...	0.035	$3 \times 10^{-12}$	Citrate + NaOH
$1.12 \times 10^{-12}$	-0.764	-0.483	0.048	0.031	...	0.043	$3 \times 10^{-12}$	Citrate + NaOH

mid-point of reduction ( $\pi_n$ ) are the observed electromotive forces of Cells b and a referred to above, subtracted from +0.337, the value assigned to the 0.1 N calomel electrode.

Under the heading "oxidation-reduction electrode" are given, first,  $\pi_n$ , the the potential at the mid-point where  $[A]/[AH_2]_T=1$ , determined for

the titration curves as described above; second,  $\Delta\pi_1$  the difference between the potential at the mid-point and at 20% reduction; and third,  $\Delta\pi_2$  the corresponding difference to 80% reduction. These two values thus give the approximate slopes of the titration curves. It will be noted that the slopes vary greatly. This is probably due to combination between the reduced and oxidized material with the formation of a substance similar to quinhydrone. Similar difficulties were encountered and corrected for by Granger and Nelson in their work on quinone. If we let  $m$  equal the fractional moles of reducing agent added and  $x$  the degree of association of the supposed complex then the value for  $\Delta\pi$  is

$$\Delta\pi = \pm 0.0295 \log \frac{1-m-mx}{m-mx}$$

The following table gives values for  $\Delta\pi$  for varying values of  $x$  when  $m=0.2$  ( $\Delta\pi_1$  in Table I).

$x$ .....	0.0	0.2	0.4	0.6	0.8	0.9
$\Delta\pi_1$ .....	0.018	0.020	0.023	0.027	0.035	0.044

A comparison of these numbers with the values for  $\Delta\pi$ , given in Table I,

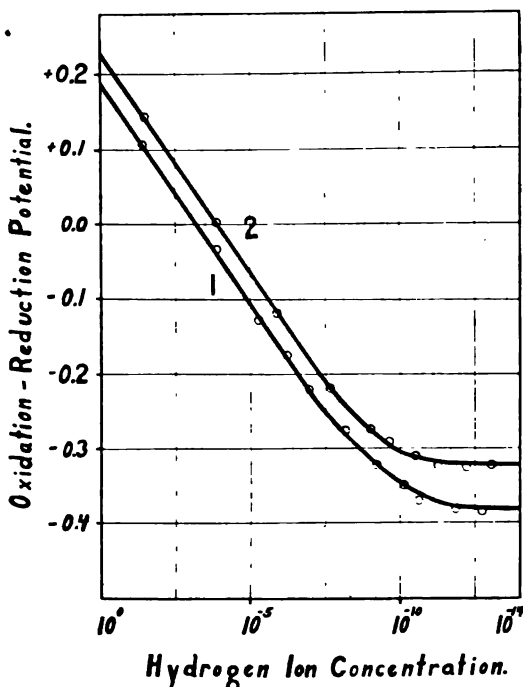


Fig. 2.

Curve 1: sodium salt of anthraquinone- $\beta$ -sulfonic acid. Curve 2: disodium salt of anthraquinone-2,6-disulfonic acid.



shows that with certain compounds, particularly in alkaline solution, the complex must be highly associated. The errors of the present method, which seem to be about 5 millivolts, make the values for  $\Delta\pi$  much less reliable than those for  $\pi_n$ . Moreover, the potential at the mid-point would not be affected by complex formation so that  $\pi_n$  is the most significant potential for theoretical discussion.

### The Potential in Acid and Alkaline Solutions

The curves shown in Figs. 2, 3, and 4 are graphical representations of the results given in Table I. The points show typical experimentally determined values of  $\pi_n$  plotted against the hydrogen-ion concentration. The smooth curve was drawn through points calculated from Equation 3.

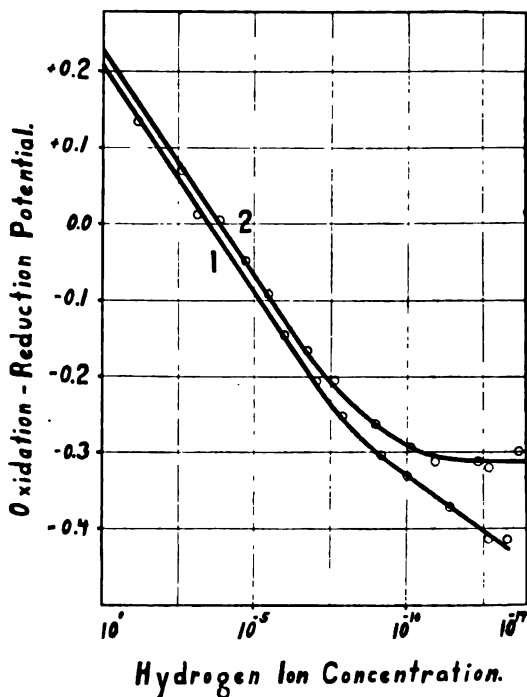


Fig. 3.

Curve 1: dicalcium salt of anthraquinone-1,8-disulfonic acid. Curve 2: disodium salt of anthraquinone-2,7-disulfonic acid.

In acid solution,  $\pi_n - \pi_h$  is obviously equal to  $\pi_0$  since, from Equations 3 and 4,  $\pi_n = \pi_0 + 0.059 \log [H^+]$  and  $\pi_h = 0.059 \log [H^+]$ . The values thus obtained for  $\pi_0$  are essentially constant (Col. 6, Table I). The last term of Equation 3 is equal to  $\pi_n - \pi_h - \pi_0$  from similar considerations; it is negligible in acid solutions.

In alkaline solution this last term of Equation 3 (Col. 7, Table I) becomes appreciable and the curve bends. In some cases the curve becomes flat showing that the term has now reduced to  $+0.0295 \log K_1 K_2 / [H^+]^2$  since  $K_2 > [H^+]$  and Equation 3 is therefore now:  $\pi_n = \pi'_0$ , the reduced form being present entirely as the divalent ion. In such cases the value for  $K_1 K_2$  can be directly calculated from Equation 4. Values for  $K_1$  may now be obtained by solving Equation 3 for each point on the bend of the graph. The values for  $K_1 K_2$  and  $K_1$  calculated in this manner are given in Col. 8 of Table I. In those instances in which the normal potential did not reach a limiting value in strongly alkaline solutions,  $K_2$  was apparently too small to be measured by this method. Its effect on the oxidation-reduction potential is obviously negligible and  $K_1$  can be directly calculated. The values of  $K_1$  and  $K_2$  thus calculated were used in drawing the curves shown in Figs. 2, 3 and 4.

The correspondence between the experimentally determined points and the curves thus drawn shows that all the results of this investigation can be expressed by Equation 3.

The reproducibility of the results and the accuracy of the method can be seen either from the points shown in the figures or by examining Table I. It is obvious that  $\pi_0$  for each substance should be constant; with a few exceptions the values agree within 10 millivolts. The values for  $K_1$  calculated from the results obtained in alkaline solutions should agree; they are given in the next to the last column; some divergence will be noted. Finally, with those compounds in which the curves become flat, the last few values of  $\pi_n$  ( $\pi'_0$ ) should be constant; they agree within the experimental error of the present method.

#### Validity of the Method

It was important to show that the reactions under investigation were strictly reversible and that the potential measured by the reduction method was the same as would be obtained from a mixture of the pure components. That the reaction is reversible is shown by the fact that the reduced vat may be oxidized by air or by ferric chloride and then reduced again to give the same potentials.

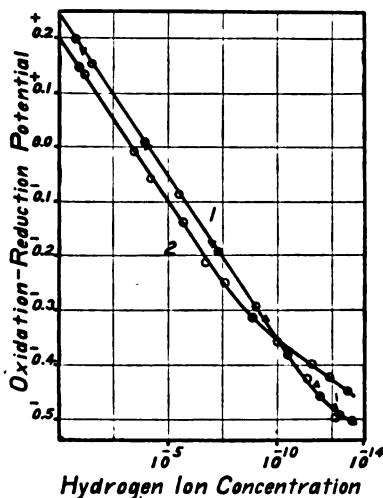


Fig. 4.

Curve 1: the 1,5-anthraquinone disulfonic acid, O = sodium salt; Δ = calcium salt. Curve 2: potassium salt of anthraquinone  $\alpha$ -sulfonic acid.

That the potential of the system is not affected by the presence of the reducing agent and its oxidation product was shown by the results of another method. This consisted in preparing a diacetyl-anthrahydroquinone-sulfonic acid which was stable in the air, hydrolyzing it to the anthrahydroquinone derivative, and measuring the potential of mixtures of this with the anthraquinone compound.

### Preparation of the Sodium Salt of Diacetyl-anthrahydroquinone- $\beta$ -sulfonic Acid

The method of preparation was similar to that used by Liebermann in preparing diacetyl-anthrahydroquinone<sup>8</sup> in which the compound was reduced and acetylated at the same time.

A mixture of 15 g. of sodium anthraquinone- $\beta$ -sulfonate, 30 g. of sodium acetate, 45 g. of zinc dust and 180 g. of acetic anhydride was heated under a reflux condenser for a few minutes, poured into 500 cc. of water and allowed to stand for 4 hours. The solution was filtered and evaporated until crystals separated out of the sirup. These crystals were filtered, washed and recrystallized from glacial acetic acid.

*Analyses.* Calc. for  $C_{12}H_{10}O_7SNa$ : Na, 5.8. Found: 5.7, 5.6. Equivalents of NaOH required for hydrolysis: 2.0. Found: 2.1, 2.1.

The potential measurement was carried out as follows. The hydrogen-ion concentration of a mixture of 250 cc. of a phosphate buffer and 100 cc. of 0.1 *N* potassium hydroxide solution was determined. Two hundred and fifty cc. of the same buffer solution was placed in the cell and 0.2 g. of the diacetyl compound was weighed into a flask so arranged that it could be swept free from oxygen and its contents later blown over into the cell with the stream of nitrogen. One hundred cc. of oxygen-free 0.1 *N* potassium hydroxide solution was run into the flask through a dropping funnel and the solution heated to boiling to effect complete hydrolysis. The solution was cooled and blown over into the cell. Successive portions of a solution containing 0.004 g. of the sodium salt of  $\beta$ -anthraquinone-sulfonic acid per cc. were run into the cell and the potential measured after each addition.

The potentials read were plotted against  $\log [A]/[AH_2]_T$  and the value of  $\pi_0$  found by interpolation. The results obtained in this and a second similar determination are

Phosphate buffer:  $\pi_A = -0.231$ ,  $\pi_B = -0.433$ ,  $\pi_0 = +0.202$

Citrate buffer:  $\pi_A = -0.051$ ,  $\pi_B = -0.249$ ,  $\pi_0 = +0.198$

Determined by the titration method (Table I)  $\pi_0 = +0.187$

The constant errors, namely, impurity of the sample, incomplete hydrolysis, and oxidation, would all tend to increase  $\pi_0$ , and a correction for them would bring the determination into closer agreement with the average value of the other method. This clearly indicates that the method of measuring oxidation-reduction potentials chosen in this investigation gives

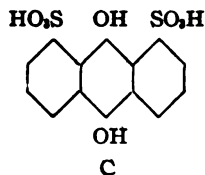
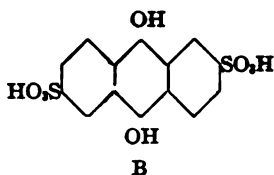
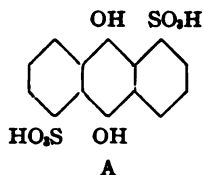
<sup>8</sup> Liebermann, *Ber.*, 21, 1172 (1888).

results comparable to those obtainable by more direct methods and that the presence of the reducing agent in no way affects the results.

### Discussion

There is nothing to indicate that the two constants used in Equation 3 are the real dissociation constants of the reduced form except that Equation 3 can be developed on this basis. It would be very desirable to obtain independent evidence of the value of  $K_1K_2$ , but this cannot be easily done.<sup>9</sup> Unquestionably anthrahydroquinone and its derivatives are very weak acids but anthrahydroquinone itself is strong enough to form a disodium salt.<sup>10</sup> The only related substance whose dissociation constants have been measured is hydroquinone; for this compound  $K_1 = 10^{-10}$ ,  $K_2$  is probably less and, therefore,  $K_1K_2$  is somewhat less<sup>11</sup> than  $10^{-20}$ . These values are of the same order of magnitude as those found for the anthrahydroquinone derivatives here investigated.

Table II summarizes the average values of the normal potentials and dissociation constants as determined by the results given in Table I. An examination of the values for  $K_1$  and  $K_2$  will show that they are entirely consistent with the structures of the compounds in question, and several regularities can be pointed out. Substitution of sulfonic acid groups in the  $\beta$  position does not markedly affect the degree of dissociation of either of the phenolic groups in the anthrahydroquinones. The values of  $K_1$  and  $K_2$  are approximately constant for the three  $\beta$  compounds;  $K_2$  is somewhat less than  $K_1$ , as would be expected. Substitution in the  $\alpha$  position, however, has a marked effect on the adjacent phenolic group, lowering its dissociation constant by about  $10^{-4}$ . Thus, in the 1,5 compound (A) which has a sulfonic acid group  $\alpha$  to both phenolic groups,  $K_1 = 10^{-12}$  and  $K_2$  is probably less than  $10^{-16}$  in contrast to the 2,6 compound (B) where  $K_1 = 10^{-8}$  and  $K_2 = 10^{-11}$ .



On the other hand, in the  $\alpha$  monosulfonic acid and the 1,8-disulfonic acid (C) the dissociation of the phenolic group farthest away from the substituent is not affected ( $K_1 = 10^{-8}$ ) but the dissociation of the hydroxyl group

<sup>9</sup> We are, of course, dealing throughout this article with the dissociation of the weak phenolic groups of the reduced compound. The sulfonic acid groups in the molecule are so strongly acidic that they can be neglected in this discussion.

<sup>10</sup> *Ann.*, 379, 37 (1911).

<sup>11</sup> *Z. physik. Chem.*, 66, 71 (1909).

which has the adjacent substituents is lowered so that it is negligible in this work (less than  $10^{-15}$ ).

The oxidation-reduction potential( $\pi_0$ ) is made more positive by about 40 millivolts by the introduction of a second sulfonic acid group in either the  $\alpha$  or  $\beta$  position. The 1,8 compound is, however, an exception to this rule, as here the increase is only about 10 millivolts. As would be expected from the properties of anthraquinone all these potentials are much lower than that recorded by Granger and Nelson for quinone, +0.695. A further discussion of the relationship between the structure of related compounds and their oxidation-reduction potentials will be deferred until the next paper, which will deal with the free and total energy changes in the reduction of anthraquinone, naphthoquinone and benzoquinone derivatives. The measurement of the temperature coefficients of the oxidation-reduction potentials of a series of such compounds is now in progress.

TABLE II  
OXIDATION POTENTIALS OF ANTHRAQUINONE SULFONIC ACIDS AND THE DISSOCIATION  
CONSTANTS OF THE PHENOLIC GROUP OF ANTHRAHYDROQUINONE SULFONIC ACID

Position of substituent	Normal potential of $AH_2(\pi_0)$ Volts	Normal potential of $A^{--}(\pi'_0)$ Volts	Dissociation constants	
			$K_1$	$K_2$
$\beta$	0.187	-0.383	$1 \times 10^{-8}$	$5 \times 10^{-12}$
2,6	0.228	-0.325	$0.8 \times 10^{-8}$	$3 \times 10^{-11}$
2,7	0.229	-0.313	$2 \times 10^{-8}$	$3 \times 10^{-11}$
$\alpha$	0.195	.....	$0.4 \times 10^{-8}$	Too
1,5	0.239	.....	$3 \times 10^{-12}$	small to
1,8	0.206	.....	$0.7 \times 10^{-8}$	measure

The authors wish to express their indebtedness to Dr. E. K. Bolton and to E. I. Du Pont de Nemours and Company for supplying them with materials and to the Cyrus M. Warren Fund of the American Academy for a grant of money for the purchase of the potentiometer.

### Summary

1. A general equation has been developed which expresses the oxidation-reduction potentials of compounds of the type of quinone in both acid and alkaline solutions.
2. The potentials of 6 anthraquinone sulfonic acids have been measured by a titration method using titanous chloride and sodium hydrosulfite. The results obtained over a wide range of hydrogen-ion concentration have been found to be in accord with the general equation as developed.
3. The validity of the experimental method has been shown by determining the potentials of mixtures of the reduced and oxidized compounds.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]  
**THE USE OF THE OXIDES OF PLATINUM FOR THE CATALYTIC  
REDUCTION OF ORGANIC COMPOUNDS. I**

BY V. VOORHEES WITH ROGER ADAMS<sup>1</sup>

Received April 10, 1923

The use of colloidal platinum and palladium and of platinum and palladium black as catalysts, especially for the reduction of organic compounds, has become very general during the past 25 years. This interest has been due chiefly to the fact that many organic substances can conveniently be prepared only by such methods. The colloidal catalysts are in general somewhat more active and are more readily prepared, but are limited in their use due to the fact that only aqueous, dil. alcoholic or dil. acetic acid solutions may be employed and that difficulty may often arise in isolating the products. On the other hand, the use of platinum or palladium black is very convenient, since almost any solvent may be employed and the product isolated merely by filtering the platinum from the reaction solution and evaporation of the solvent. Of platinum and palladium, the former has been much more commonly used and is the one which will be discussed in this communication.

The method of preparation of platinum and palladium black, however, has not been given the study which it deserves. The earlier methods for making platinum black are very numerous and do not yield a product which is very active as a catalyst in the reduction of organic compounds.

O. Loew<sup>2</sup> first described the preparation of a satisfactory catalyst for organic reductions and his method, except for slight changes by other investigators, is the one which is used almost exclusively at the present time. Loew's method consists in the treatment of an aqueous chloroplatinic acid solution with formaldehyde and then precipitation of platinum black by the addition of alkali. The product is filtered, dried *in vacuo* and exposed to air or oxygen before being used. His directions have been changed, chiefly in regard to the temperature of precipitation and the nature of the alkali, first by Willstaetter and Hart;<sup>3</sup> again, by Willstaetter and Waldschmidt-Leitz;<sup>4</sup> and still again by Feulgen.<sup>5</sup> These changes from the original directions of Loew result in the production of a more effective catalyst and eliminate a few of the experimental difficulties involved, such as that of filtration of the platinum black. Moreover, it is reported that the platinum produced by the modified directions is more uniform in its activity as a catalyst. Even with these improvements, the production of a very active catalyst cannot be relied upon unless the directions are followed with exactness. Drying in a good vacuum for 24 to 48 hours is very necessary if a high activity is to be obtained.

<sup>1</sup> This paper is an abstract of a thesis by V. Voorhees presented in partial fulfillment of the requirements for the degree of Master of Science in chemistry at the University of Illinois.

<sup>2</sup> Loew, *Ber.*, **23**, 289 (1900).

<sup>3</sup> Willstaetter and Hart, *ibid.*, **45**, 1472 (1912).

<sup>4</sup> Willstaetter and Waldschmidt-Leitz, *ibid.*, **54**, 113 (1921).

<sup>5</sup> Feulgen, *ibid.*, **54**, 360 (1921).

In this laboratory where catalytic reductions have been studied for the past few years, it has often been found that various students, using the same directions for making the catalyst, do not obtain a platinum of like activity. The investigation which is described here was carried out in order to determine whether a simpler and more reliable method could be found for the preparation of a highly active platinum catalyst.

A brief description of the characteristics of a catalytically active platinum black is given below, since these observations led to the experiments and results which are now being reported. The presence of oxygen in platinum black is necessary for its activity as a catalyst in the hydrogenation of organic compounds. This has been noted by numerous investigators<sup>6</sup> and tested quantitatively by Willstaetter and Waldschmidt-Leitz.<sup>7</sup> In fact, the activity of platinum black seems to depend almost entirely upon the amount of oxygen absorbed. Willstaetter believes that the presence of oxygen is also necessary for catalysis with colloidal platinum, but recent work by Skita<sup>8</sup> has shown quite conclusively that this is not the case.

The form in which absorbed oxygen is present in the platinum black has been a question of great interest to chemists. Wöhler<sup>9</sup> has shown convincingly that when platinum black absorbs oxygen there are formed true oxides or hydroxides of platinum. These consist for the most part of platinumous oxide or, in the presence of water, platinumous hydroxide, and a certain amount of platinic dioxide and its hydrate. From his experiments it is indicated that the platinumous oxide or hydroxide is the active catalyst, or at least is an intermediate product in the formation of the active catalyst. This conclusion was drawn after a very careful study of platinum black which had absorbed oxygen and a comparison of its properties with those of the various oxides of platinum. Platinum black prepared by the usual method shows by its activity that it contains about 10 to 18% of platinumous oxide and a few per cent. more of the higher oxides of platinum. The reactivity of the platinum ceases immediately as soon as the oxygen present has disappeared. It is well known that in catalytic reductions the oxygen in the platinum is not immediately removed by the hydrogen but reacts only gradually during a considerable period of time. When the oxygen in the platinum does become very small in amount the

<sup>6</sup> *Öfversikt Finska Vetenskaps-Soc. Förh.*, 57, 267 (1900); *Z. angew. Chem.*, 39, 24 (1904); *Gazz. chim. ital.*, 34, 57 (1904); *Ber.*, 51, 767 (1918); *Compt. rend.*, 158, 409 (1914); *Ber.*, 51, 768 (1918); *Akad. Wetenschappen Amsterdam Proc.*, 29, 424 (1917).

<sup>7</sup> Ref. 4. In this paper an excellent review is given of the various papers on the mechanism by which the oxygen activates the platinum as a catalyst. See also *Ber.* 55, 573 (1922).

<sup>8</sup> Skita, *ibid.*, 55, 139 (1922).

<sup>9</sup> Wöhler, *ibid.*, 36, 3475 (1906).

reduction slows down or stops altogether. It is merely necessary, however, to agitate the platinum with oxygen or air in order to revivify it.

The state of division of a platinum catalyst is also important and recent modifications in the preparation of platinum black have had as one of their objects the formation of a more finely divided product. It is most probable that the state of division and the absorption of oxygen go hand in hand.

From these properties of platinum black it was concluded that the oxides of platinum, if prepared in a finely divided state, would be as effective catalysts in hydrogenation as any which could possibly be produced. They would be distinctly more active than the best platinum black since the maximum amount of oxygen in the latter as platinum oxides, is at the most only about 20%. Provided the oxide is finely divided, it would probably make little difference what particular oxide of platinum is used, since the hydrogen would reduce the higher oxides to the lower oxide, presumably the active catalyst. If these oxides are usable, even though they may be merely as active as ordinary platinum black, they would have a distinct advantage over it because of the ease with which many of them may be prepared. For example, certain tedious details such as the careful drying of platinum black could be eliminated. Also the oxides of platinum, since the oxygen is present, could be used when wet, while platinum black precipitated from solution must be thoroughly dried and exposed to the air for the absorption of oxygen before it becomes most active as a catalyst. Experiments fully substantiate the predictions; many of the oxides of platinum are more effective as catalysts than platinum black made by the usual method.

All of the various oxides of platinum described in the literature are now being studied as catalysts. Of these, platinous hydroxide formed as described by the method of Thompson<sup>10</sup> has been made already. This compound is a catalyst and about as active as ordinary platinum black. The necessary conditions of precipitation and the physical characteristics of the product, however, are not ideal and this probably accounts for its lack of great activity. It seemed likely that a proper fusion method might be more suitable for the formation of a finely divided oxide which might be easily handled. Yorgensen<sup>11</sup> has already described a poorly defined oxide of platinum produced by the fusion of sodium chloroplatinate with sodium carbonate. Such a method would hardly be expected to produce an active catalyst since the temperature of such a fusion mixture must reach 850° or over. Such high temperatures are known to interfere often with the activity of a catalyst. Moreover, it has been shown by Wöhler<sup>9</sup> that both platinous oxide and platinic dioxide decompose fairly

<sup>10</sup> Thompson, *J. prakt. Chem.*, [2] 15, 294 (1876).

<sup>11</sup> Yorgensen, *ibid.*, [2] 16, 344 (1877).



rapidly when held for any length of time at a temperature of  $450^{\circ}$ . The most appropriate method conceivable for the formation of an oxide of platinum is the one used so often for the oxides of other metals, namely, the fusion of the nitrate.<sup>12</sup> In the case of platinum, this may be carried out by fusing chloroplatinic acid and sodium nitrate. Since sodium nitrate fuses at  $312^{\circ}$ , ideal conditions are obtainable. It is actually found that an extremely active oxide of platinum is thus produced and this is now being compared with platinum black and with oxides made in various ways. Preliminary results indicate that this is a higher oxide of platinum, possibly platinum trioxide. A more detailed description of this substance and its chemical properties will be given in a communication that will appear soon.

When the ordinary commercial chloroplatinic acid crystals are treated with an excess of sodium nitrate and fused, an evolution of nitrogen dioxide takes place and a precipitate forms in the melt. Upon cooling and washing with water, the new oxide of platinum is obtained. It is brown in color but the shade varies with the change in conditions during fusion. The whole procedure is extremely simple and within half an hour a large amount of catalyst can be prepared for use.

The formation of this oxide of platinum is not limited to a fusion of chloroplatinic acid with sodium nitrate, but may be produced by the fusion with nitrates of other metals. Moreover, low-melting salts of certain other acids may be used with success. The amount of the salt used for the fusion and the temperature employed have a decided effect upon the nature of the catalyst. All of these conditions are now being studied quantitatively and will be reported later.

The new catalyst seems to be less sensitive toward poisons than ordinary platinum black. It has, however, the same disadvantage as platinum black when used for the reduction of readily oxidizable compounds. Much of the oxygen in the catalyst is probably removed, due to the oxidation of the substance to be reduced. Platinum is formed which is only slightly reactive until shaken again with air or oxygen. The solvent used for the substance to be reduced affects the speed of reduction.

The catalyst has already been used for the reduction of phenol and certain substituted phenols to hexahydrophenols, for certain pyridine derivatives to piperidine derivatives, of vanillin and salicyl aldehyde to the corresponding alcohols, of aromatic nitro compounds to amines, of methyl-

<sup>12</sup> No one has attempted to prepare an oxide of platinum by such a method. The nearest approach lies in the work of Davy, who found that platinum sulfide dissolves in fuming nitric acid and that when this solution is evaporated to dryness and the residue treated with alcohol, platinum black is produced (*Phil. Mag.*, 1820, 330). Hittorf also found that a brown oxide of platinum is formed by electrolytic oxidation of platinum when platinum strips are used as electrodes in a bath of fused potassium or sodium nitrate (*Pharm. Zentr.*, 1848, 23).

ethyl ketone to *sec.* butyl alcohol, and of certain heterocyclic compounds to the corresponding saturated derivatives. From these results, it may be concluded that this catalyst will probably work for all cases where platinum black can be used. All of these reductions mentioned were carried out with hydrogen under a pressure of 1.5 to 3 atm., but it is inconceivable that this has any more effect with this catalyst than with ordinary platinum black.

The method of procedure for the reduction of compounds consists, in general, of dissolving in a suitable solvent the compound to be reduced, adding the catalyst, removing the air, and then treating with hydrogen. As soon as the hydrogen is introduced and the reaction mixture is shaken, the brown catalyst becomes black, due, presumably, to the reduction of the higher oxide to a lower one. The time necessary for this change of the catalyst depends to a considerable extent upon the way in which the catalyst has been formed and on the nature of the solvent used. For the catalyst, the preparation of which is described in this paper, the time necessary varies from a few seconds to 15 or 20 minutes. As soon as it becomes black it either becomes spongy in appearance or takes on a finely divided form which readily remains suspended in the reaction mixture. The platinum which is now present is essentially the same as a very active platinum black made in the usual way and is similar in all its properties. In many cases the reduction will take place so rapidly that the reaction mixture will actually become hot, but the speed of reduction depends upon the nature of the compound which is being studied. When the reduction is complete, the suspended platinum can be made to settle merely by shaking the reaction mixture with air for a short time, after which it may be readily filtered off or the solution may be decanted. After an amount of catalyst has reduced so much of the unsaturated compound that it has lost the greater part of its activity, it may be revived by shaking a short time with air just as is customary when using platinum black.

It is obvious that the oxide of platinum prepared as described is not a catalyst in itself, but is converted by the hydrogen into the lower oxide which presumably is the active catalyst. In the study of the various oxides of platinum there is, therefore, a third condition which must be observed in the preparation, namely, that a product is formed which is readily reduced by hydrogen to the active catalyst. It was observed that when the sodium nitrate and chloroplatinic acid are fused at a temperature of 700° or higher, an oxide is formed which catalyzes the reduction of organic substances only slowly; moreover, in certain instances, from 1 to 2 hours is required before the brown oxide turns black and becomes active as a catalyst.

The oxides of palladium and iridium are formed in a similar manner to

the oxide of platinum, and an investigation of these products as catalysts which has shown them to be very active, is now being continued.

### Experimental

**Preparation of the Oxide of Platinum.**—In a 150 cc. porcelain casserole or Pyrex beaker, is prepared a solution of crystals of chloroplatinic acid corresponding to 1 g. of platinum in 5 cc. of water. To this is added 20 g. of sodium nitrate. The mixture is heated gently over a Bunsen flame and stirred with a glass rod while the water is expelled. The mixture is then heated until complete fusion takes place, which requires a temperature of about  $300^{\circ}$ . Brown oxides of nitrogen are evolved at about  $320^{\circ}$  and a brownish powder precipitates in the fusion mixture. It is advisable to continue the stirring during the fusion in order to prevent spattering and to prevent caking of the precipitate on the bottom of the casserole. The melt is kept hot until the copious evolution of nitrogen oxides has almost ceased, a process which requires from 5 to 15 minutes, depending upon the temperature at which the fusion mixture is held. This point is easily observed, however, as there is a sudden decrease in amount of gases given off, although the brown fumes never cease completely even after the precipitation of the oxide seems to be complete. The mass is now allowed to cool and then treated with 50 cc. of water. The brown precipitate settles to the bottom and can be washed by decantation once or twice and then washed on a filter until free from nitrates as shown by the absence of the ferrous sulfate test. This requires about 100 to 125 cc. of water. Toward the end of the washing there may be traces of oxide that tend to be carried through. It is desirable, therefore, to keep the filtrates. The filtration and washing are readily completed in 15 to 20 minutes. The product that is thus obtained may either be used directly or may be dried in a desiccator and kept until needed.

**Discussion of Reaction.**—In studying the best conditions under which the fusion may be carried out, a platinum thermocouple was used for determining the temperature of the fusion mixture. It was observed that the higher the temperature used during the fusion, the more complete was the precipitation of the platinum. On the other hand, the product formed is not as active a catalyst as that produced at lower temperatures. It seems advisable to use a temperature about  $450^{\circ}$  if the best results are to be obtained. At  $600^{\circ}$  and  $700^{\circ}$  the product seems to be slightly more yellow in color and causes the reduction of various organic compounds to take place much more slowly. It is quite unnecessary, however, to record the temperature in the preparation. A small flame just sufficient to cause the fusion to take place as mentioned, will invariably give very satisfactory results.

The filtrate, after the separation of the catalyst from the fusion mixture, should be evaporated to dryness. The small amount of platinum which always remains may then be precipitated quantitatively by adding a few grams of sodium carbonate and fusing at a comparatively high temperature. The melt is then cooled and the platinum recovered by washing free from the salts.

It is advisable always to test for platinum in all the filtrates before discarding any of them since there is a tendency for a small amount of the platinum to remain in solution. A very satisfactory and delicate test for platinum, described by Wöhler,<sup>13</sup> consists in making the solution acid with hydrochloric acid and adding a few drops of stannous chloride. A yellow color develops when platinum is present and a brown color when it is in large amount. If any doubt exists as to whether the solution is yellow, it should be shaken with a small amount of ether, under which conditions the yellow color concentrates in the upper layer, thus indicating the presence of platinum.

The oxide may be dried rapidly by washing several times with alcohol. If this is carried out, however, care must be taken to prevent exposure to the air since spontaneous combustion will take place.

If organic matter is present in the chloroplatinic acid such as is generally the case when recovered platinum is used, it will be oxidized during the fusion and seems to have no deleterious effect.

The oxide may be produced by using a much smaller proportion of sodium nitrate to chloroplatinic acid than that suggested. With the larger quantity, however, filtration of the oxide takes place more readily with practically no tendency to become colloidal and pass through the filter.

There always remains in the casserole or beaker a thin film of oxide which cannot be removed by the ordinary means. This is dissolved best by treating with a little constant-boiling hydrobromic acid, which immediately dissolves it. The solution thus obtained may then be added to the next fusion mixture.

There is always a certain amount of the oxide which remains sticking to the filter paper during filtration, so that these papers should be ignited and the residue added to any platinum catalyst which has already become inactive and requires redissolving and reprecipitation.

**Apparatus.**—The general form of apparatus employed in the reduction experiments is that described by Skita<sup>14</sup> and modified by Lochte, Noyes and Bailey.<sup>15</sup> As a container for hydrogen a Prest-o-lite tank was used from which the filling had been removed. The top of the tank contains two openings. In one of these is welded a tube holding a gage and valve;

<sup>13</sup> Wöhler, *Chem. Ztg.*, 31, 938 (1907).

<sup>14</sup> Skita, *Ber.*, 45, 3589 (1912).

<sup>15</sup> Lochte, Noyes and Bailey, *THIS JOURNAL*, 43, 2601 (1921).

through this tube the hydrogen from a large cylinder is introduced into the tank. In the second opening is welded another tube with two outlets, each of which holds a needle valve. These outlets are so arranged that it is possible to shut off the tank from either outlet. One is used for the vacuum and the second for a tube leading to the reaction-mixture bottle. The Prest-o-lite tank is so calibrated that merely by reading the fall in pressure and the temperature, the amount of hydrogen absorbed by the reaction mixture can be quite closely determined. The connection between the Prest-o-lite tank and hydrogenating bottle may be a copper tube connected to a heavy taped rubber tube which is in turn connected to a glass tube inserted through the stopper of the bottle. The rubber tube and stopper should be high grade and must be carefully boiled with alkali before being used.

**Reduction Experiments.**—It has been found that the speed of reduction of various organic compounds is approximately proportional to the amount of catalyst used. It therefore follows that in the experiments described, the speed can be greatly increased by using more catalyst.

In the preparation of vanillyl alcohol from vanillin, several amounts of material have been reduced in succession, with the same platinum. The reduction of successive amounts of the other substances has not been attempted, but would undoubtedly take place just as satisfactorily.

The experiments described below were carried out under an initial pressure of hydrogen of 2.75 atm., so that an exact comparison can be made among the various experiments.

In each case, the reduction of about 95% of the material takes place rapidly; the speed of reduction then slows down. The reduction of the last 5% often requires almost as much time as is necessary for the reduction of the first 95% of material.

The products are isolated in every case by shaking with air, in order to cause the platinum to settle, filtering or decanting the solution. The product may then be either distilled *in vacuo* or crystallized, according to its physical properties.

**Vanillin to Vanillyl Alcohol.**—A solution is made of 20 g. of vanillin in 100 cc. of alcohol and 0.5 g. of catalyst is added. The reduction is complete in about 50 minutes after which the reaction mixture is shaken with air, the solution decanted and a second 20 g. of vanillin in 100 cc. of alcohol added. The second reduction requires about 110 minutes, a third of a similar nature, 125 minutes, and a fourth about 120 minutes.

**Ethylmethyl Ketone to *sec.* Butyl Alcohol.**—Eighty g. of ethylmethyl ketone is treated with 0.5 g. of catalyst. The reduction is complete in about 4 hours and practically a quantitative yield of product may be isolated.

**Phenol to Cyclohexanol.**—A solution is made of 62 g. of phenol in 50 cc. of alcohol and 0.65 g. of catalyst is added. The time necessary for complete reduction is 6.5 hours and a yield of 54 g. of pure cyclohexanol is obtained. A trace of benzene can be detected by its odor.

**Salicyl Aldehyde to Saligenin.**—A solution is made of 30 g. of salicyl aldehyde in 60 cc. of alcohol and 0.25 g. of catalyst is added. The reduction is complete in about 75 minutes and practically a quantitative yield is obtained.

**Nicotinic Acid Hydrochloride to Nipocotinic Acid Hydrochloride.**—A solution is made of 10 g. of nicotinic acid hydrochloride in 150 cc. of water and 1.0 g. of catalyst is added. The reduction is complete in about 2 hours. The product may be isolated by vacuum evaporation of the solution.

### Summary

1. Since experiments indicate that the oxygen which must always be present in platinum black if it is to be an active catalyst, is present in the form of an oxide of platinum, it was concluded that the oxides of platinum should be excellent catalysts. These are being studied.

2. An oxide of platinum has been formed by the fusion of chloroplatinic acid with sodium nitrate and has proved to be an excellent catalyst.

3. Various types of organic compounds such as phenols, pyridine derivatives, aromatic and aliphatic aldehydes and heterocyclic compounds have been reduced. The speed of reduction with this catalyst is greater than when ordinary platinum black is used.

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### NOTE

**Vanillin Glyceride.**—The attention of the writer was recently called to a deposit which had formed in a flavoring mixture consisting essentially of alcohol, glycerin, and vanillin. The precipitate was easily purified by filtration and washing with water and, thus isolated, was a white, almost odorless, micro-crystalline powder, slightly soluble in water and ether. It was moderately soluble in cold alcohol, easily on heating, separating from solution on cooling in distinct crystalline plates. It was also easily soluble in 0.5 *N* potassium hydroxide solution, without, however, showing any definite neutralization, and was precipitated in crystals on the addition of acid, behaving thus like a phenol.

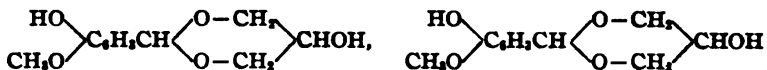
On warming the crystals with water, they dissolved slowly and the odor of vanillin became apparent. After a few hours' heating, vanillin alone crystallized from the cooled solution, and in the mother liquor glycerin was found by the usual tests. The hydrolysis was greatly hastened by acid catalysts, and an approximate analysis of the compound was made as follows.

2.0795 g. of substance was mixed with 20 cc. of warm water, and 1 cc. of 0.5 *N* hydrochloric acid added. The crystals dissolved immediately, and vanillin separated. To insure a complete hydrolysis, the mixture was heated for 1 hour at 90–100°. On cooling, the solution was extracted 4 times with ether, in 10cc. portions. The ether extract, evaporated to constant weight at 50°, was nearly pure vanillin; the aqueous solution similarly evaporated left a residue of slightly discolored glycerin.

Calc. for vanillin: (1 mol.) 67.25%. Found: 1.405 g., or 67.5%.

Calc. for glycerin: (1 mol.) 40.71%. Found: 0.818 g., or 39.3%.

The substance is evidently the result of a combination of vanillin and glycerin in molecular proportions, with elimination of one molecule of water, and has probably one of the following two structural formulas.



It would thus be analogous to the acetals and glucosides and, in fact, a quite similar compound from benzaldehyde and glycerin has been described by Fischer.<sup>1</sup> The free phenol group accounts for the acidic nature and, at the same time, the absence of a free aldehyde group explains why the acid properties are less marked than in the case of vanillin.

Experiments on the preparation of the compound from its constituents showed that the reaction between vanillin and glycerin was much accelerated by the presence of mineral acid, but the latter was a very disturbing factor during the isolation of the product. Working in the cold and as rapidly as possible, it was found impossible to free the crystals from mother liquor before a very considerable hydrolysis had occurred, and any trace of acid left in the preparation caused its complete decomposition in a short time. To secure a stable product, it was found advisable to dissolve the crude crystals in a slight excess of 0.5 *N* alkali, and reprecipitate by somewhat less than the equivalent amount of acid, thus leaving the mother liquor slightly alkaline. After washing free from alkali, the crystals thus obtained appear to be permanent. Where time is no object, the preparation without acid is perhaps simpler.

For example, a mixture of 5 g. of vanillin, 25 g. of glycerin, 15 g. of alcohol, and 2 g. of 30% hydrochloric acid was allowed to stand at ordinary temperature. After 3 days the formation of crystals was noticed. After 10 days the crystals were filtered, washed with cold water, and dried in a desiccator. Five days later the preparation, amounting to 2.45 g., was found to be entirely decomposed into vanillin and glycerin.

A similar mixture with 1.5 g. of 90% sulfuric acid in place of the hydrochloric acid yielded after 3 weeks 2.95 g., or 59% of the vanillin used, which after careful purification as described proved to be stable. The same mixture without any acid yielded after 11 weeks 1.83 g., or 36.6%.

Vanillin glyceride melts, not very sharply, at 160–162°. On adding a little acid to a dilute (about 0.2 *N*) alkaline solution, it crystallizes slowly in distinct plates which, under the microscope, in convergent polarized light, show an orthorhombic interference figure. Axial angle,  $2E = 90-100^\circ$ . Birefringence, positive: dispersion,  $r < v$ .

When the crystals are touched with a drop of dil. hydrochloric acid they quickly disappear and on standing, or on slow evaporation, the characteristic monoclinic needles of vanillin are observed.

<sup>1</sup> Fischer, *Ber.*, 27, 1536 (1894).

The writer hopes to be able to report later on the reaction of glycerin with other aromatic aldehydes.

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FRANCIS D. DODGE

**The Carbohydrate Content of Navy Beans.**<sup>1</sup>—In a recent paper, Peterson and Churchill<sup>2</sup> have reported upon the carbohydrate content of the navy bean (*Phaseolus vulgaris*). Closely similar figures were obtained in work done by the writer several years ago.

The methods used in the two investigations were much the same—including separation of the carbohydrates by successive alcohol and cold water extraction, and enzyme digestion. Thus, closely agreeing figures were obtained in the two pieces of work for total sugars, dextrins, starch, pentosans and crude fibre.

Among the differences, in methods and results, it should be stated that Peterson and Churchill determined pentosans in several different fractions, the writer only on the whole bean. It is possible therefore that the figures in the later method for dextrin and starch really include a small amount of pentosans.

In the method under discussion the carbohydrate obtained by enzyme hydrolysis was subtracted from the carbohydrate obtained by acid hydrolysis of the residue—from the cold water extraction and the result called "insoluble hemicellulose," giving a figure considerably higher than that obtained by the Wisconsin Investigators by boiling their malt extract residue with 1% hydrochloric acid. Unlike the other workers the writer was never able to obtain mucic acid when attempting to determine galactans. It was not known whether this failure was due to the absence of galactans or to the method used.

A table comparing most of Peterson and Churchill's results with those of the writer is given below.

It was noted with interest that some of the difficulties encountered in manipulation were much the same. This was especially true with reference to fineness of grinding, filtering, time and completeness of digestion. In the present work it was found that bean flour passing a 100-mesh sieve gave more satisfactory results than flour passing a larger mesh sieve. The fat, for instance, was more easily and completely extracted with the fine flour than with the coarse flour. This complete extraction of the fat decreased the difficulties encountered in filtering the later extracts.

<sup>1</sup> The work reported in this article was conducted at the Nutrition Laboratory, Department of Home Economics, University of Chicago. It formed part of a thesis submitted in partial fulfilment of the requirements for the degree of Master of Science in the University of Chicago, June, 1919.

<sup>2</sup> Peterson and Churchill, *THIS JOURNAL*, 43, 1180 (1921).



Composition of navy beans (*Phaseolus vulgaris*)

	Peterson and Churchill	Eichelberger
Moisture.....	12.96	10.08
Ash.....	3.88	3.43
Ether extract.....	1.83	2.36
Protein ( $N \times 6.25$ ).....	18.42	22.69
Alcohol soluble carbohydrate as dextrose (total sugar).....	1.59	2.61
Dextrins.....	3.71	3.23
Starch.....	35.20	35.22
Insoluble hemicelluloses, by difference....	....	8.90
Hemicelluloses.....	(.83)*	....
Pentosans.....	8.37	(8.08)*
Galactans.....	1.33	....
Crude fibre.....	3.94	3.62
Organic acids, waxes, etc., by difference...	8.77	7.86
	100.00	100.00

\* Not included in summation, since it is included with the item above.

Here, as in Peterson's work, the blue coloration with iodine during enzyme digestion disappeared very slowly. However, the author found that after 17 hours' digestion with commercial pancreatin, under a layer of toluol, the coloration completely disappeared and constant results for enzyme digestion were obtained.

In conclusion, I wish to express my sincere thanks to Dr. Katherine Blunt, of the University of Chicago, for her personal interest and careful supervision of this work.

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MARIETTA EICHELBERGER

## NEW BOOKS

An Introduction to the Analytical Chemistry of the Rarer Elements. By LOUIS J. CURTMAN, Assistant Professor of Chemistry, Chief of the Division of Qualitative Analysis, College of the City of New York. Privately printed, New York, 1921. 64 pp. 21 × 14.5 cm. Price \$1.25.

This small book, according to the preface, "is designed to lay a sound foundation for the analytical study of the rarer elements" and the author has made a careful selection of experiments to accomplish this result. It is a source of satisfaction to know that "every experiment was personally performed by the author." It is undoubtedly of advantage to have all reagents and test solutions of known strength, although in practice with natural and industrial products the problem may not be so conveniently arranged for us.

The reviewer has long been convinced of the importance of this group of elements and has for many years advocated its more careful study; therefore to his mind such books as the above are highly commendable.

No one can fail to profit by the use of the material in this brief treatise, but a previous study of the mineral sources and the extraction therefrom, together with an elementary study of the absorption spectra of the rare earth group would add much to the value of the work described.

PHILIP E. BROWNING

**Laboratory Manual of Organic Chemistry.** By HARRY L. FISHER, formerly Instructor in Organic Chemistry, Columbia University; in charge of Research Division, the B. F. Goodrich Co. John Wiley and Sons, New York, N. Y.  $\frac{1}{2}$  + 331 pp. 21 figures. 14.5  $\times$  22 cm.

"This book is the outgrowth of almost ten years of intensive laboratory teaching. Practically all of the laboratory experiments, in mimeograph form, have been in the hands of three different classes of students, day, night, and summer, each year for over five years, and during this time have been repeatedly corrected." This introductory statement shows how this laboratory manual comes to be so remarkable in many ways. It is all that other manuals of its kind are and, in addition, it contains many new and valuable features. Besides many of the more usual experiments, it contains the following: Grignard reaction, acetals, *l*-menthone and its oxime, lecithin from egg yolk, ethyl isocyanate, glycocoll from hippuric acid, mucic acid from lactose, hydrocinnamic acid, permanganate oxidation, limonene dihydrochloride, camphor from pinene, and anthraquinone. Much emphasis is put on the proper handling and setting up of apparatus. The many clear figures help to impress on the student this important phase of organic work. The questions at the ends of the chapters are varied from the "obvious" things which are missed by the poorer students to matters which will call for considerable thought from even the best students. Throughout, the book is aimed at all types of students. Its directions are minute, almost painfully so at times, and of such a nature that the poorest student can follow them and get results. At the same time the text is interspersed with many references to the original literature which cannot but be inspiring to the better students who have the time and ability to use them. It may be mentioned that many of these references are from the latest journals. Such, for instance, are those on removing "frozen" stopcocks, and on preparing ethylene for mustard gas. The second part of the book contains over 100 pages on organic combustions. Here the directions are the most minute and detailed to be found anywhere except in the larger reference books. On first reading, these directions give a wrong impression of the methods. The apparatus for the determination of nitrogen, illustrated on p. 276, really works very simply when the directions have been mastered by carrying out the process

once or twice. The chief criticism which can be made against this unusual manual is that most of the processes used are not the simplest possible. However, almost all of the complications introduced, are of considerable educational value. Their introduction would be of disadvantage only in courses where quality must be sacrificed for the sake of speed.

FRANK C. WHITMORE

**Lunge-Berl. Chemisch-technische Untersuchungsmethoden.** Edited by Ing.-Chem. DR. ERNST BERL, Professor of Technical Chemistry and Electrochemistry at the Technischen Hochschule, Darmstadt. Julius Springer, Berlin, 1921. Vol. I, Seventh Edition, xxxii + 1099 pp. 291 fig. 15.5 × 23.5 cm. Price M 294.

This is the first volume of a new edition of Lunge completely revised and enlarged. The preface states that 1915 had been set for its appearance, but that the World War interfered. The plan of the book is the same as in the earlier editions, that is, the various chapters are written by experts in the several fields.

The following headings from the table of contents show the scope of the present volume. Sampling, General Operations of the Laboratory, Volumetric Analysis, Analysis by Electrical Conductivity Measurement, Gas Analysis, Hydrometry, Manometers and Anemometers, Heat Measurement, Colorimetry, Calculation of Analysis, Technical Gas Analysis, Microchemical Analysis, and Electrolytic Analysis. The discussion of the above list of topics covers over 400 pages and constitutes an admirable presentation of the general points of technical analysis.

The list of special methods includes those used in the examination of solid and liquid fuels, water both for drinking and industrial purposes and the raw materials, by-products and finished products of the manufacture of sulfurous, sulfuric, nitric, hydrochloric and hydrofluoric acids. The chlorine and soda industries are treated in the same way. Potash salts and liquefied and compressed gases have chapters and an appendix deals with methods of analyzing bromine, saltpeter and potash products.

The text contains numerous illustrations and there is a portrait of Lunge as a frontispiece. Literature references, including even a few American ones, are copious. Numerous tables of data useful in the calculation of analytical results accompany the book in a separate packet. These tables are printed on one side only to permit mounting for easy reference in the laboratory.

The reviewer can commend the work most heartily to those who either as teachers or as commercial chemists need to have at hand a comprehensive book on technical analysis.

C. W. FOULK







